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MATHEMATICS

Continuous Games with Perfect Information

by
A. ZIĘBA

Presented by H. STEINHAUS on July 2, 1955

This paper contains an elementary example of an open (i. e. a not strictly determined) continuous game. H. Steinhaus has discovered continuous games and introduced the fundamental notions [1]. An elementary exposition of the theory of continuous games is to be found in [2] (cf. also [3]). Here we do not repeat the definitions generally used in the theory of games: the meaning of the fundamental theorem can be understood from the proof even without any knowledge of the notions used in its formulation. Open games have been investigated by Gale, Mycielski, Stewart and Zięba [4], [5]. The appropriate definitions will be found in their works.

Assume that, at the moment $t=0$, two elements, P and E, are at points $x_P(0)$ and $x_E(0)$ of a real half-axis $x(0 \leqslant x < \infty)$; the elements P and E can move on the axis with the velocities $\dot{x}_P$ and $\dot{x}_E$ respectively, so that we have the following relations, satisfied for every $t \geqslant 0$:

(i) $\gamma \leqslant \dot{x}_P(t) \leqslant \delta$,

(ii) $\alpha \leqslant \dot{x}_E(t) \leqslant \beta$,

the numbers $\alpha, \beta, \gamma, \delta, x_P(0), x_E(0)$ satisfy the inequalities

(iii) $0 < \alpha < \beta < \gamma < \delta$,

(iv) $0 \leqslant x_P(0) < x_E(0)$.

From conditions (i)—(iv) it follows that for every pair of trajectories $x_P(t)$, $x_E(t)$ satisfying those conditions there exists exactly one number T such that

$$x_P(T) = x_E(T). \tag{1}$$

This common position of the elements P and E at the moment T will be denoted shortly by x_T. Elements P and E will be interpreted as

pawns. The players who control them will be denoted by the same symbols, P and E (P-pursuing, E-escaping). For player P the method of play will be given by any equation of the form

$$\frac{dx_P}{dt} = f_P(x_P, x_E), \tag{2}$$

where the function figuring on the right side is of the class C^2 and satisfies the inequalities

$$\gamma \leqslant f_P \leqslant \delta.$$

The method of play for player E is defined in an analogical way:

$$\frac{dx_E}{dt} = f_E(x_P, x_E). \tag{3}$$

Next, assume that the half-axis $0 \leqslant x < \infty$ is split into two disjointed sets, A_P and A_E, giving the whole axis when summed up.

In any play the players choose their methods independently. A pair of trajectories, $x_P(t)$ and $x_E(t)$, correspond exclusively to those methods (the initial conditions being taken into account); a point x_T corresponds exclusively to those trajectories.

If point x_T belongs to the set A_P, player P wins. If point x_T belongs to the set A_E, player E wins.

THEOREM. *If the set A_P is dense in the set A_E and vice versa, then the game P is open.*

Proof. It is sufficient to show that for every method of player E there exists a method of player P using which he wins the play, and that for every method of player P there exists a method of player E, using which he wins the game. We shall prove the first of the above properties. The proof of the second is similar. Let the equation

$$\frac{dx_E}{dt} = f_E(x_P, x_E)$$

be the method of player E. Let player P use the following method:

$$\frac{dx_P}{dt} = \frac{\gamma + \delta}{2} = a. \tag{4}$$

Denote by T_a the time T corresponding to these methods. If $x_{T_a} \in A_P$, the theorem is proved. Therefore suppose that $x_{T_a} \in A_P$. Let us consider the following one-parametric family of pursuit methods (we are interested only in small values of the parameter ε):

(5) player P uses method (4) until he finds himself at a point whose distance from point x_{T_a} is ε. Then he alters his method to

$$\frac{dx_P}{dt}=a+\varepsilon\ ^{*)}.$$

At this final stage player E will make use of the equation

$$\frac{dx_E}{dt}=f_E\left(\left\{at+\varepsilon\left[t-\left(T_a-\frac{\varepsilon}{a}\right)\right]\right\},x_E(t)\right), \tag{6}$$

and not, as before, of the equation

$$\frac{dx_E}{dt}=f_E\big(\{at\},x_E(t)\big). \tag{7}$$

The function f_E has, by hypothesis, bounded first and second derivatives in an arbitrary neighbourhood of point x_{T_a}. Accordingly, for t contained in the interval $T_a-\varepsilon\leqslant t\leqslant T_a$, the right sides of equations (6) and (7) differ by small quantities of the order ε^n where $n\geqslant 2$.

Thus, finally, the trajectories of player P, corresponding to method (4) and its variant (5), differ by small quantities of the order ε^2, while the trajectories of player E differ by small quantities of a higher order than 2.

Besides, since by hypothesis the curve $x_E(t)$ (in view of (ii) and (iii)) intersects the straight line $x=x_{T_a}$ at an angle greater than any positive value, the point x_T cannot remain unchanged in passing from method (4) to method (5). (Fig. 1) (Point x_T is a projection parallel to the straight line $x=x_{T_a}$ of the intersection point of the trajectories of the elements P and E). This point is, of course, a continuous function of the parameter ε. Moreover, in an arbitrary neighbourhood of the point x_{T_a} there exist points belonging to the set A_P.

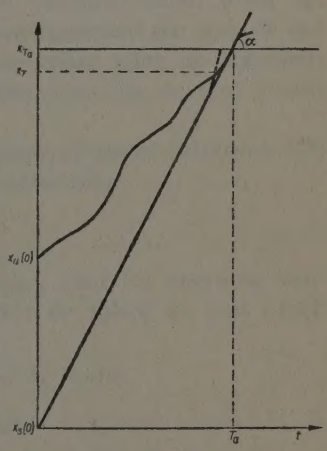

Fig. 1

Thus there exists such an ε_0 that point x_T, corresponding to method (5) for $\varepsilon=\varepsilon_0$, belongs to the set A_P.

INSTITUTE OF MATHEMATICS, POLISH ACADEMY OF SCIENCES

*) The trajectory of player P has, in passing from methods (4) to (5), an angular point, which is inadmissible. This difficulty can easily be overcome by smoothing the trajectory in a suitable neighbourhood of that point on the arc by lengths of the order of ε^3.

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BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Cl. III — Vol. III, No. 10, 1955

MATHÉMATIQUE

Sur la definition de Łojasiewicz de la valeur d'une distribution dans un point

par

Z. ZIELEŹNY

Présenté par S. MAZUR le 3 Août 1955

Nous considérons les distributions d'une variable réelle. Nous désignons les distributions, avec Mikusiński, symboliquement par $f(x)$, ce qui met en évidence l'analogie des formules avec celles pour les fonctions ordinaires. Cela étant, le sens de la distribution $f(\alpha x+\beta)$, où α et β sont des nombres ($\alpha\neq 0$), est clair.

S. Łojasiewicz a proposé de définir la valeur d'une distribution $f(x)$ au point x_0 comme la limite au sens de distributions

$$\lim_{\alpha\to 0} f(\alpha x+x_0),$$

pourvu que cette limite existe. Il est clair que, pour les fonctions continues $f(x)$, cette notion coïncide avec la notion de valeur au sens usuel.

Nous démontrerons le

THÉORÈME. *Si $f(x)$ est une distribution et la limite*

$$g(x)=\lim_{\alpha\to 0} f(\alpha x+x_0)$$

existe, la distribution $g(x)$ est une fonction constante *).

Ce théorème montre que la valeur d'une distribution peut être interprétée toujours comme un nombre (égal à la valeur de la fonction constante $g(x)$).

Il résulte aussitôt de la définition que la limite $g(x)$ satisfait à l'équation

$$g(\lambda x)=g(x) \quad \text{pour tout} \quad \lambda\neq 0. \tag{1}$$

Le théorème est donc une conséquence directe du lemme suivant:

LEMME. *Si une distribution $g(x)$ satisfait à l'équation* (1), *elle est une fonction constante.*

*) Une autre démonstration de ce théorème a été annoncée par S. Łojasiewicz; cette démonstration n'a pas été publiée.

Il résulte de (1) que $g(x)$ est une distribution d'ordre fini; elle peut donc être représentée comme une dérivée $G^{(k)}(x)$ d'ordre k d'une fonction continue $G(x)$. La dérivation est ici entendue au sens de distributions. La fonction

$$\Phi_\lambda(x) = \lambda^k G(x) - G(\lambda x) \tag{2}$$

est un polynôme de degré $\leqslant k-1$.

$$\Phi_\lambda(x) = a_{k-1}(\lambda)x^{k-1} + \ldots + a_0(\lambda); \tag{3}$$

cela est trivial pour $\lambda = 0$ et résulte de l'égalité

$$\Phi_\lambda^{(k)}(x) = \lambda^k g(x) - \lambda^k g(\lambda x) = 0$$

pour $\lambda \neq 0$.

Nous démontrerons que

$$a_j(\lambda) = c_j(\lambda^j - \lambda^k) \qquad (j = 0, \ldots, k-1), \tag{4}$$

où c_j sont des nombres.

On a, d'après (2),

$$\Phi_{\mu\lambda}(x) = \Phi_\lambda(\mu x) + \lambda^k \Phi_\mu(x)$$

et, par comparaison des coefficients,

$$a_j(\mu\lambda) = a_j(\lambda)\mu^j + a_j(\mu)\lambda^k \qquad (j = 0, \ldots, k-1). \tag{5}$$

En particulier,

$$a_0(\mu\lambda) = a_0(\lambda) + a_0(\mu)\lambda^k;$$

pour $\mu = 0$, on a

$$a_0(\lambda) = a_0(0)(1 - \lambda^k).$$

Si $j > 0$, on a, en substituant $\mu = \lambda = 0$ et $\mu = \lambda = 1$,

$$a_j(0) = a_j(1) = 0.$$

Lorsque $a_j(\lambda) \equiv 0$, $a_j(\lambda)$ est évidemment de la forme (4). Lorsque, au contraire, $a_j(\lambda_0) \neq 0$ pour un nombre λ_0, ce nombre λ_0 est différent de 0 et de 1. En substituant $\mu = \lambda_0$ dans (5), il vient

$$a_j(\lambda_0\lambda) = a_j(\lambda)\lambda_0^j + a_j(\lambda_0)\lambda^k;$$

d'autre part, en substituant $\lambda = \lambda_0$ et remplaçant μ par λ, il vient

$$a_j(\lambda_0\lambda) = a_j(\lambda_0)\lambda^j + a_j(\lambda)\lambda_0^k,$$

d'où

$$a_j(\lambda) = \frac{a_j(\lambda_0)}{\lambda_0^j - \lambda_0^k}(\lambda^j - \lambda^k),$$

ce qui prouve (4).

En vertu de (2), (3) et (4), on conclut, en posant $x = 1$, que $G(x)$ est un polynôme de degré $\leqslant k$. Par conséquent, la distribution $g(x) = G^{(k)}(x)$ est une fonction constante.

INSTITUT MATHÉMATIQUE DE L'ACADÉMIE POLONAISE DES SCIENCES

BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Cl. III — Vol. III, No. 10, 1955

MATHÉMATIQUE

Sur les solutions de l'équation différentielle $x^{(n)}+A(t)x=0$ qui satisfont à des conditions données dans plusieurs points

par
E. KRZYWICKA

Présenté par S. MAZUR le 12 Septembre 1955

On considère, dans cette note, la question d'existence et d'unicité, lorsque les valeurs de la solution ou de ses dérivées sont prescrites dans $r(r\leqslant n)$ points différents $a_1<\ldots<a_r$. Soient données r suites croissantes de nombres naturels $\leqslant n$

$$j_{\mu 1}, j_{\mu 2}, \ldots, j_{\mu q_\mu} \quad (\mu=1,\ldots,r;\ q_1+q_2+\ldots+q_r=n) \tag{1}$$

et n nombres réels $c_{\mu\nu}$. On suppose qu'une solution $x(t)$ de l'équation

$$x^{(n)}+A(t)x=0, \tag{2}$$

où $A(t)$ est une fonction continue $\neq 0$, satisfait à n conditions

$$x^{(j_{\mu\nu}-1)}(a_\mu)=c_{\mu\nu}. \tag{3}$$

Les points $a_1,\ldots,a_r$ et les nombres $q_1,\ldots,q_r$ étant fixés, l'existence d'une solution unique de (2) *satisfaisant aux conditions* (3) *ne dépend pas du choix des suites* (1) *ou des nombres $c_{\mu\nu}$.*

Si une solution de (2) satisfaisant à (3) existe et est unique pour toute suite croissante $a_1,\ldots,a_r$, nous dirons que les conditions du type $(q_1,\ldots,q_r)$ *déterminent univoquement cette solution.*

Les conditions du type $(q_1,\ldots,q_r)$ déterminent univoquement la solution de (2) *lorsque*

(a) $A(t)>0$ *et les nombres $q_2,\ldots,q_r$ sont pairs,*

ou

(b) $A(t)<0$ *et les nombres $q_2,\ldots,q_{r-1}$ et q_r+1 sont pairs.*

Lorsque l'équation (2) est d'ordre $\leqslant 6$ et $A(t)<0$ les conditions de la dernière proposition sont non seulement suffisantes, mais aussi nécessaires.

Les propositions précedentes généralisent certains théorèmes *) de Švec [1]. Leurs démonstrations s'appuyent sur des théorèmes de Mikusiński [2], [3] et de Kneser [4].

Les résultats présentés dans cette note ont été obtenus sous la direction du Professeur J. Mikusiński.

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*) Les théorèmes 2 et 4 (plus précisément la première partie du théorème 4) du travail [1] et certains corollaires concernant l'équation $x^{(n)}+A(t)x=0$ qui sont énoncées sans démonstrations, sont des cas particuliers de notre seconde proposition.

BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Cl. III — Vol. III, No. 10, 1955

THEORETICAL PHYSICS

General Solutions for the Diffraction of a Dipole Field by a Perfectly Conducting Wedge

by

R. TEISSEYRE

Presented by L. INFELD on August 26, 1955

1. We recently submitted the method for solving the problem of diffraction of a dipole field by a perfectly conducting wedge [7]. The method given was a generalization and to some degree a modification of the Senior method [5] for the diffraction by a conducting halfplane.

In the present paper are given general solutions for the electromagnetic field of an arbitrary electric or magnetic dipole in the case of a conducting wedge.

Although the outer angle of the wedge $\varkappa$ is assumed to be greater than π, the method is nevertheless true for any angle.

2. The following notations are used.

The edge of the wedge is coincident with z (i. e. x_3) axis (Fig. 1).

Co-ordinate of field: $P(x_k)=P(r,\theta,z)$ $k=1,2,3,$

Co-ordinate of dipole: $Q(x_k^0)=Q(r_0,\theta_0,z_0)$.

$$\theta_0+\theta=\varphi_1, \qquad \theta_0-\theta=\varphi_2,$$

$$R_\varrho=\sqrt{r^2+r_0^2+2rr_0\cos\varrho+(z-z_0)^2},$$

$$R=\sqrt{r^2+r_0^2-2rr_0\cos\varphi_2+(z-z_0)^2},$$

$$S=\sqrt{r^2+r_0^2-2rr_0\cos\varphi_1+(z-z_0)^2},$$

$$T=\sqrt{r^2+r_0^2-2rr_0\cos(\varphi_1-2\varkappa)+(z-z_0)^2}.$$

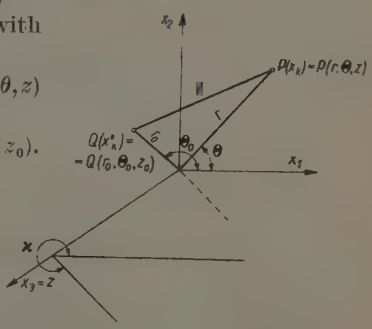

Fig. 1

R, S, T are the distances from the point of field P in relation to the dipole, to the image of the dipole in the upper surface of the wedge, and to the image in the lower one.

By $P(0)$ is denoted the path of integration which is the steepest descent path passing through the point 0 in a complex plane (Fig. 2).

ε_{krs} is the full antisymmetrical tensor; its values are ± 1 when k, r, s are even or odd permutations of the number 1, 2, 3; in other cases ε_{krs} equals zero. δ_{ks} equals unity or zero respectively when $k=s$ or $k \neq s$. The other quantities have the following definitions:

$$T_{ks}^{(l)} = \begin{pmatrix} (-)^{l-1}\cos(\varrho+\varphi_l) & (-)^{l-1}\sin(\varrho+\varphi_l) & 0 \\ \sin(\varrho+\varphi_l) & -\cos(\varrho+\varphi_l) & 0 \\ 0 & 0 & (-)^l \end{pmatrix},$$

$$\delta_{ks}^{*} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$C_{ks} = \begin{pmatrix} \cos 2\varkappa & \sin 2\varkappa & 0 \\ \sin 2\varkappa & -\cos 2\varkappa & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

By $\delta(\ldots<\ldots)$ is denoted, when the inequality given in the brackets is fulfilled, the quantity equal to unity, and in the opposite case, the quantity equal to zero. The electromagnetic field of an electric dipole is denoted by (E_k^e, H_k^e), and the field of a magnetic dipole by (E_k^m, H_k^m).

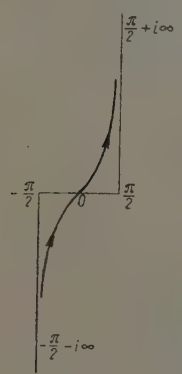

Fig. 2

The field (E_k^e, H_k^e) is derived from the Hertz vector Π_s^e of an electric dipole as follows:

$$E_k^e = \left(\frac{\partial^2}{\partial x_k \partial x_s} + k^2\delta_{ks}\right)\Pi_s^e$$

$$H_k^e = ik\varepsilon_{krs}\frac{\partial}{\partial x_r}\Pi_s^e,$$

the field (E_k^m, H_k^m) is thus derived from Π_s^m:

$$E_k^m = ik\,\varepsilon_{krs}\frac{\partial}{\partial x_r}\Pi_s^m$$

$$H_k^m = -\left(\frac{\partial^2}{\partial x_k \partial x_s} + k^2\delta_{ks}\right)\Pi_s^m.$$

In the following, the amplitudes of the Hertz vector are denoted by A_s^e and A_s^m.

The factor $e^{i\omega t}$ is omitted throughout.

3. Below is given first the field of an electric dipole:

$$E_k^e = \frac{\sin\frac{\pi^2}{\varkappa}}{4\varkappa i} A_s^e \int\limits_{P(0)} d\varrho$$

$$\sum_{l=1,2}' \left[\left((-)^{l-1}\frac{\partial^2}{\partial x_k \partial x_s^0} + k^2 T_{ks}^{(l)}\right)\frac{e^{-ikR_\varrho}}{kR_\varrho}\,\frac{1}{\sin\frac{\pi}{2\varkappa}(\varrho+\varphi_l+\pi)\sin\frac{\pi}{2\varkappa}(\varrho+\varphi_l-\pi)}\right] +$$

$$
\begin{aligned}
(1)\qquad & + \delta(\theta < \pi + \theta_0)\, A_s^e \left(-\frac{\partial^2}{\partial x_k \partial x_s^0} + k^2 \delta_{ks} \right) \frac{e^{-ikR}}{kR} + \\
& + \delta(\theta < \pi - \theta_0)\, A_s^e \left(\frac{\partial^2}{\partial x_k \partial x_s^0} - k^2 \delta_{ks}^* \right) \frac{e^{-ikS}}{kS} + \\
& + \delta(2\varkappa - \theta_0 - \pi < \theta)\, A_s^e \left(\frac{\partial^2}{\partial x_k \partial x_s^0} - k^2 C_{ks} \right) \frac{e^{-ikT}}{kT}.
\end{aligned}
$$

$$
H_k^e = \frac{\sin \frac{\pi^2}{\varkappa}}{4\varkappa i} A_s^e \int d\varrho
$$

$$
\begin{aligned}
& \sum_{l=1,2} \left[ik\varepsilon_{krp} \frac{\partial}{\partial x_r} T_{ps}^{(l)} \frac{e^{-ikR_\varrho}}{kR_\varrho} \frac{1}{\sin \frac{\pi}{2\varkappa}(\varrho + \varphi_l + \pi) \sin \frac{\pi}{2\varkappa}(\varrho + \varphi_l - \pi)} \right] + \\
(2)\qquad & + \delta(\theta < \pi + \theta_0)\, A_s^e ik\varepsilon_{krs} \frac{\partial}{\partial x_r} \frac{e^{-ikR}}{kR} + \\
& - \delta(\theta < \pi - \theta_0)\, A_s^e ik\varepsilon_{krp} \delta_{ps}^* \frac{\partial}{\partial x_r} \frac{e^{-ikS}}{kS} + \\
& - \delta(2\varkappa - \theta_0 - \pi < \theta)\, A_s^e ik\varepsilon_{krp} C_{ps} \frac{\partial}{\partial x_r} \frac{e^{-ikT}}{kT}.
\end{aligned}
$$

The first term of these expressions gives the pure diffraction field; the following three terms represent the geometrical optic field — the field directly from a dipole and from the images in the surfaces of the wedge. The discontinuities of the geometrical optic field are of course compensated by the discontinuities of the pure diffraction field. It may also be shown that the electromagnetic field given by (1) and (2) has an admissible singularity $(rr_0)^{-1/2}$ on the edge of the wedge.

In operating with formulas (1) and (2), the following rules are of value

$$
C_{ps} \frac{\partial}{\partial x_p} T = -\frac{\partial}{\partial x_s^0} T, \qquad \delta_{ps}^* \frac{\partial}{\partial x_p} S = -\frac{\partial}{\partial x_s^0} S, \qquad \frac{\partial}{\partial x_s} R = -\frac{\partial}{\partial x_s^0} R
$$

and in the interior of the integrals the operator's equality:

$$
\varepsilon_{3rp} \frac{\partial}{\partial x_r} T_{ps}^{(l)} = -\varepsilon_{3rs} \frac{\partial}{\partial x_r^0}
$$

can be applied.

The above remarks are also true of the field of a magnetic dipole:

$$
E_k^m = \frac{\sin \frac{\pi^2}{\varkappa}}{4\varkappa i} A_s^m \int d\varrho
$$

$$
\sum_{l=1,2} \left[(-)^l ik\varepsilon_{krp} \frac{\partial}{\partial x_r} T_{ps}^{(l)} \frac{e^{-ikR_\varrho}}{kR_\varrho} \frac{1}{\sin \frac{\pi}{2\varkappa}(\varrho + \varphi_l + \pi) \sin \frac{\pi}{2\varkappa}(\varrho + \varphi_l - \pi)} \right] +
$$

$$+\delta(\theta<\pi+\theta_0)\,A_s^m ik\,\varepsilon_{krs}\frac{\partial}{\partial x_r}\frac{e^{-ikR}}{kR}+$$

$$+\delta(\theta<\pi-\theta_0)\,A_s^m ik\,\varepsilon_{krp}\,\delta_{ps}^*\frac{\partial}{\partial x_r}\frac{e^{-ikS}}{kS}+$$

$$+\delta(2\varkappa-\theta_0-\pi<\theta)\,A_s^m ik\,\varepsilon_{krp}\,C_{ps}\frac{\partial}{\partial x_r}\frac{e^{-ikT}}{kT}.$$

$$H_k^m=\frac{\sin\frac{\pi^2}{\varkappa}}{4\varkappa i}A_s^m\int d\varrho$$

$$\sum_{l=1,2}\left[\left(\frac{\partial^2}{\partial x_k\partial x_s^0}-(-)^l k^2 T_{ks}^{(l)}\right)\frac{e^{-ikR_\varrho}}{kR_\varrho}\,\frac{1}{\sin\frac{\pi}{2\varkappa}(\varrho+\varphi_l+\pi)\sin\frac{\pi}{2\varkappa}(\varrho+\varphi_l-\pi)}\right]+$$

$$+\delta(\theta<\pi+\theta_0)\,A_s^m\left(\frac{\partial^2}{\partial x_k\partial x_s^0}-k^2\delta_{ks}\right)\frac{e^{-ikR}}{kR}+$$

$$+\delta(\theta<\pi-\theta_0)\,A_s^m\left(\frac{\partial^2}{\partial x_k\partial x_s^0}-k^2\delta_{ks}^*\right)\frac{e^{-ikS}}{kS}+$$

$$+\delta(2\varkappa-\theta_0-\pi<\theta)\,A_s^m\left(\frac{\partial^2}{\partial x_k\partial x_s^0}-k^2 C_{ks}\right)\frac{e^{-ikT}}{kT}.$$

A full account of this work, together with approximate formulas for short wave lengths, will be given in Acta Physica Polonica.

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CHIMIE

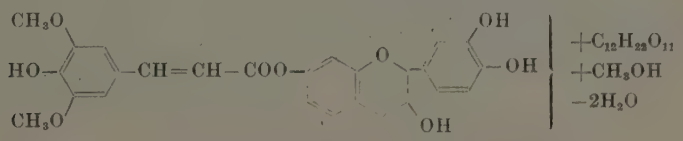
Recherches sur le colorant du choux rouge (*Brassica oleracea*)

par

J. CHMIELEWSKA, I. KAKOWSKA et B. LIPIŃSKI

Présenté par W. LAMPÉ le 17 Juin 1955

Les recherches faites par un des nous dans les années 1930—1936 ont permis d'établir la composition du colorant du choux rouge—chlorure de rubrobrassicine. Ce colorant contient: une molécule de cyanidine esterifiée par une molécule d'acide sinapique; deux molécules de glucose et un groupe O-methylique, stable dans un milieu alcalin, très labile dans un milieu acide [1], [2]. On n'a pas pu constater comment les substituants sont liés entre eux et c'est pourquoi pour le chlorure de rubrobrassicine on s'est arrété en 1936 à la formule suivante:

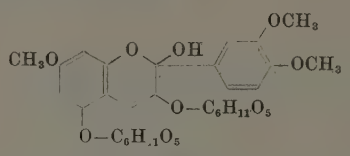


(I)

En partant de la détermination comparative de T. Miłobędzki et W. Szczypiński du *pH* correspondant au changement de la coloration du colorant selon qu'il contient ou ne contient pas une molécule d'acide sinapique, on a admis que l'acide sinapique est lié avec le groupe phénolique de l'aglucone et non pas avec le groupe alcoolique du sucre [3]. Le chlorure de rubrobrassine, — premier produit de la dégradation du colorant même, qui consiste dans la séparation de l'acide sinapique du colorant, ressemble plus à la mécocyanine qu'à la cyanine, ce qui permet de supposer la présence du sucre comme biose. La labilité du groupe méthoxyle, inconnue jusqu'à présent dans le groupe d'anthocyanines, n'a pas pu trouver son explication.

Dans les recherches poursuivies actuellement pour établir la structure du colorant du choux rouge on s'est servi du blocage des groupes

phénoliques libres avec le diazométhane. Comme ce réactif n'a pas été appliqué jusqu'à présent aux anthocyanines, on a commencé par méthyler la cyanine et on a démontré que l'éther triméthylique de la base flavyle, c'est à dire 3′, 4′ 7-triméthylcyanine (II), résulte de la méthylation de ce colorant contenant de l'eau de cristallisation avec du diazométhane en suspension dans l'éther.



(II)

Comme résultat de la méthylation du chlorure de rubrobrassicine dans des conditions analogues, on a obtenu un produit contenant 6 groupes méthoxyles, dont 3 se trouvaient dans le colorant primaire et les 3 autres furent introduits au cours de la méthylation.

Analyse. Trouvé: 20,6%, 20,2% OCH_3

pour $C_{42}H_{55}O_{21}$ 6 groupes OCH_3 calculé: 20,9%.

Cela prouve que dans le colorant du choux rouge se trouvent 3 groupes phénoliques libres dont un fait partie de l'acide sinapique et les deux autres se trouvent dans l'aglucone.

L'hydrolyse alcaline du colorant obtenu (la séparation de l'acide 3, 4, 5-triméthoxycinnamique) donne l'éther diméthylique de rubrobrassine.

Analyse. Trouvé: 12,7%, 13,0% OCH_3

pour $C_{30}H_{37}O_{16}Cl$ 3 groupes OCH_3 calculé: 13,5%.

Par l'action de diazométhane à ce composé s'associe encore un groupe méthylique. Il en résulte l'éther triméthylique de rubrobrassine, identique au produit de la méthylation directe du chlorure de rubrobrassine.

Analyse. Trouvé: 17,8%, 18,2% OCH_3

pour $C_{31}H_{40}O_{17}$ 4 groupes OCH_3 calculé: 18,1%.

Ces résultats sont la preuve chimique directe que l'acide sinapique dans une molécule du colorant du choux rouge est lié avec un groupe phénolique de l'aglucone. La coloration bleue du chlorure de rubrobrassicine avec Cl_3Fe, démontrant la présence des groupes OH libres dans les positions 3′, 4′, indique que l'acide sinapique est combiné avec un des groupes phénoliques de l'anneau chromyle.

Pour trouver le groupe auquel le sucre est lié, on appliqua la méthanolyse au lieu de l'hydrolyse. On a obtenu l'aglucone contenant un groupe OCH_3.

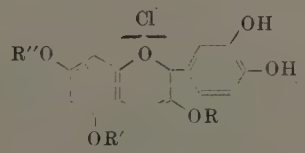
Analyse. Trouvé: 8,7%, 8,9% OCH_3

pour $C_{16}H_{13}O_6Cl$ 1 groupe OCH_3 calculé: 9,2%.

La méthanolyse n'ayant pas été employée jusqu'à présent pour les anthocyanines, on procéda d'une manière analogue à la méthanolyse du chlorure de cyanine pour établir si la méthylation de l'aglucone n'a pas lieu au cours de la réaction. Cette séparation, aussi bien que l'hydrolyse, donna le chlorure de cyanidine. Cela indique que le groupe OCH_3 de l'aglucone du colorant du choux rouge qui se détache au cours de l'hydrolyse reste, au contraire, intact pendant la méthanolyse et que le composé obtenu représente un éther monométhylique de cyanidine inconnu jusqu'à présent. On l'a nommé rubrobrassidine.

Les traits caractéristiques du chlorure de rubrobrassidine qui le distinguent du monoéther de cyanidine naturel connu (chlorure de péonidine) sont: la coloration bleue avec Cl_3 Fe, la solubilité très marquée dans l'eau et la dissociation du groupe méthylique pendant le chauffage avec l'acide chlorhydrique dilué.

Comme la partie chromyle de la cyanidine contient seulement 3 groupes OH capables d'être substitués, les résultats obtenus indiquent que 2 molécules de glucose sont présentes sous forme de biose et que dans le chlorure de rubrobrassicine tous les trois groupes hydroxyles de l'anneau chromyle sont substitués: le premier (phénolique) — par une molécule de l'acide sinapique, le deuxième (phénolique ou celui de l'anneau hétérocyclique) — par le groupe méthylique, le troisième (phénolique ou celui de l'anneau hétérocyclique) — par la glucobiose, ainsi que le montre la formule (III).

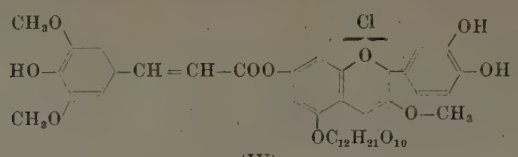


(III)

Dans les positions des substituants les combinaisons suivantes sont possibles:

1. R — biose; R' — CH_3; R'' — acide sinapique;
2. R — biose; R' — acide sinapique; R'' — CH_3;
3. R — CH_3; R' — biose; R'' — acide sinapique;
4. R — CH_3; R' — acide sinapique; R'' — biose.

Vu la solubilité très marquée dans l'eau du chlorure de rubrobrassicine, le schéma 3 (Formule IV) semble être le plus probable.



(IV)

Actuellement, on continue les recherches pour confirmer par des preuves chimiques directes la formule (IV) proposée pour le chlorure de rubrobrassicine.

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CHEMISTRY

Azeotropic and Polyazeotropic Systems. XXI. A Series of Saddle Azeotropes Formed by Acetic Acid, Pyridine and Paraffinic Hydrocarbons

by

K. ZIĘBORAK

Presented by W. ŚWIĘTOSŁAWSKI on August 18, 1955

1. Introductory remarks

Some years ago Świętosławski [1], [2] classified negative binary and positive-negative azeotropes with no water as component. Since 1951, a number of ternary systems belonging to the latter group have been investigated in our department, but only a few numerical data have been published [3], [4], [5]. The present publication concerns a series of saddle azeotropes which are formed in ternary systems consisting of one non-polar component (a normal paraffinic hydrocarbon) and of two polar components, these being acetic acid and pyridine forming a binary negative azeotrope [(−)(A, P)].

2. Experimental metods and substances used

In the present investigations, the method of ebulliometric measurements was used [2], [5]; a three stage differential Świętosławski's ebulliometer was applied [7]. Sufficiently pure and dehydrated acetic acid and pyridine were prepared. Normal paraffins were prepared from syntine fraction by removing unsaturated hydrocarbons and submission to two successive fractional distillations. Further details concerning the method will be published in Roczniki Chemii.

3. Results obtained

First to be investigated was the ternary system composed of *n*-heptane, acetic acid and pyridine, in which the formation of a saddle azeotrope was proved. Table I gives numerical data concerning this system. They show some improvement on those published in a previous publi-

cation [3]. Fig. 1 represents the projection of the top-ridge line on the concentration triangle in this system, together with a probable location of the bottom concavity line joining two points corresponding to the composition of the two positive azeotropes $[P, H_1]$ and $[A, H_1]$ boiling at $t_{P,H}$ and $t_{A,H}$.

Next, in the same way, the system composed of n-octane, acetic acid and pyridine, as shown in Fig. 2, was examined by Brzostowski [8]. In this system, not only is the location of top-ridge line designed by the

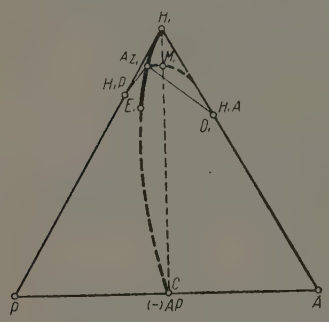

Fig. 1

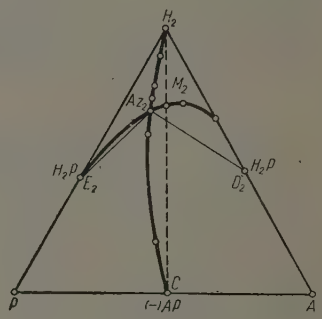

Fig. 2

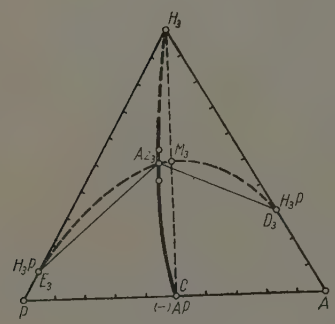

Fig. 3

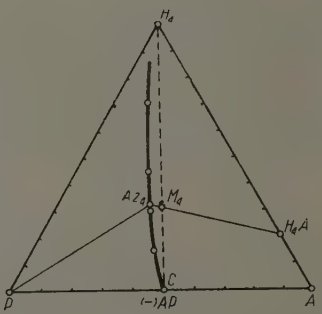

Fig. 4

Figs. 1—4. A series of ternary diagrams. On each of the concentration triangles, A, P and H represent acetic acid, pyridine and one of the paraffinic hydrocarbons of series (H). H_1 is n-heptane, H_2 n-octane, H' n-nonane, H_3 n-decane. At the same time, the three sides of the triangle represent the projections of the boiling temperature isobars examined by the use of the ebulliometric method. Points E, D, and C correspond to the concentration of two binary positive azeotropes and one negative. The line joining H with C is called the main line. This coincides with the projection of the boiling temperature isobars obtained for mixtures of $[(-)(A, P)]$ with H. For designating the minimum boiling temperature on this isobar, symbol M is used. $HAzC$ is the projection of the top-ridge curve on the concentration triangle. Point Az represents the composition of the ternary positive-negative azeotrope.

method described by Świętosławski [2], but also the shape of the bottom concavity isobar $E_2Az_2M_2D_2$ was ebulliometrically examined. The composition of the saddle azeotrope in this and further systems was then ascertained by means of a fractional distillation of an appropriately chosen mixture. The composition of the fractions collected were verified by complete chemical analysis.

The system composed of *n*-nonane, acetic and pyridine, was investigated by Drozdowska [8]. In this system the binary azeotrope composed of *n*-nonane and pyridine is almost tangent. It is characterized by the azeotropic depression of 0.22°C. The projection of the top-ridge line CAz_3H_3 on the concentration triangle APH_3 is, as in the previous systems, slightly shifted from the main line CH_3 towards the left side of the triangle. The system composed of *n*-decane, acetic acid and pyridine was examined by Turski [8]. It is characterized by one binary positive azeotrope $[H_4A]$ and one positive zeotrope $[H_4P]$. In spite of the latter, a saddle azeotrope Az_4 was found, as shown in Fig. 4.

We were able to prove that *n*-undecane also forms a ternary positive-negative azeotrope with acetic acid and pyridine; we found, however, that the substances used in these experiments were not sufficiently pure. This system will be reexamined once more and the numerical data will undergo verification.

In Table I are listed the boiling temperatures and compositions of the ternary positive-negative azeotropes $[(-)(A,P)(+)H_i]$, examined, the latter being expressed both in weight and mole per cent.

TABLE I

Boiling temperatures and compositions of positive-negative azeotropes

Name of system	Boiling temp. of saddle azeotrope in °C.	Composition — weight per cent			Composition — mols per cent		
		A	P	H_i	A	P	H_i
Acetic acid—pyridine and *n*-heptane *)	96.5	3.1	10.6	85.0	5.0	12.8	82.2
n-octane	115.7	10.4	20.1	69.5	16.6	24.6	58.8
n-nonane	128.0	20.9	29.3	49.8	31.2	33.6	35.2
n-decane	134.1	31.4	38.2	30.4	43.0	39.6	17.0

*) values verified and somewhat changed.

Table II shows the compositions and boiling temperatures of corresponding binary azeotropes. As regards the azeotropes formed by acetic

acid and a series of normal paraffins, Kurtyka's data [6] were used. The boiling temperature isobars formed by pyridine with corresponding paraffins were examined by ourselves.

TABLE II

Binary positive azeotropes of pyridine and acid with normal paraffinic hydrocarbons

System of azeotropes (P, H_i) and (A, H_i)	Azeotrope boiling temperature – °C	Composition-weight per cent H_i	Composition-mols per cent H_i
Pyridine and			
n-heptane	95.5	74.7	70.0
n-octane	109.5	43.9	35.0
n-nonane	115.1	10.1	6.5
n-decane	zeotropic mixture		
Acetic acid and			
n-heptane	91.8	67.0	55.1
n-octane	105.8	47.0	31.8
n-nonane	113.0	31.0	17.5
n-decane	116.95	20.5	9.9

4. Discussion of results

In Fig. 5 are given the composition in weight percentages of a series of ternary positive-negative and binary azeotropes. In Fig. 6, all binary and ternary saddle azeotropes examined are together graphically represented on a single diagram, the weight percentages being replaced by molar ones. It can be readily seen that the points corresponding to the compositions of the saddle azeotropes lie on a common curve $Az_1Az_2Az_3Az_4$ and that the straight lines drawn through the points representing the concentrations of binary (A, H_i) and ternary $(\pm)Az_i$ azeotropes, cross at a common point Z' (Fig. 6).

The composition of positive-negative azeotropes changes with the boiling temperature of corresponding hydrocarbons. Certain important regularities are obvious. The concentration of acetic acid in a series of azeotropes appears as a linear increase, while the change in the concentrations of pyridine and the corresponding paraffinic hydrocarbons is shown graphically in the form of a curve similar in shape to a parabole (Fig. 7).

The boiling temperature range of hydrocarbons forming positive-negative azeotropes with acetic acid-pyridine, may be approximately determined by extrapolation of the data given in Figs. 6 and 7. This range is located approximately between 90°C. and 200°C. A more detailed

analysis of experimental data, which, in view of exigencies of space, can but be touched on in this paper, shows that the compositions and boiling temperatures of mixtures represented by points lying on the

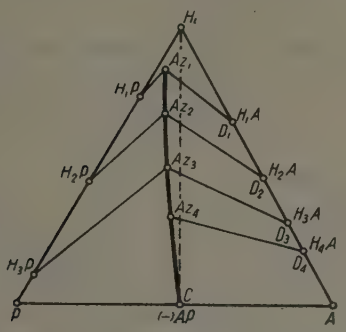

Fig. 5. A series of ternary saddle azeotropes $[(-)(A, P), (+)(H_i)]$ formed by A-acetic acid, P-pyridine, H_i — n-paraffinic hydrocarbons;

(H_1P), (H_2P), (H_3P), (H_1A), (H_2A), (H_3A), (H_4A), $[(-)(A, P)]$

binary azeotropes; $(\pm)Az_i$ — compositions of the saddle azeotropes in weight per cent.

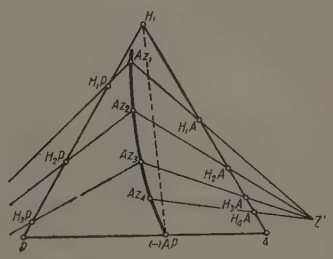

Fig. 6. A series of ternary saddle azeotropes. The compositions are expressed in mole per cent. A detailed explanation of symbols is given at Fig. 5.

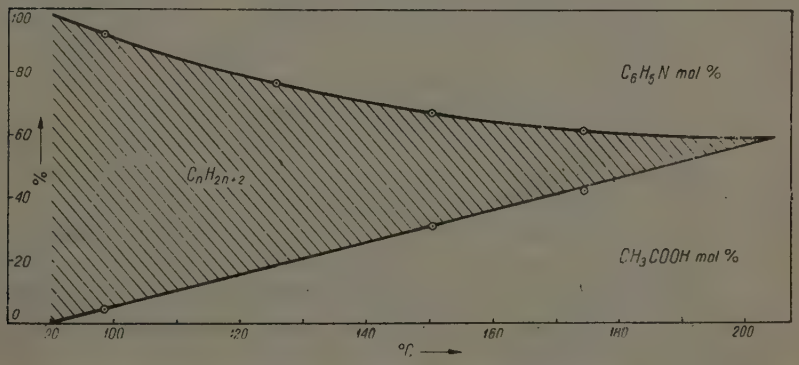

Fig. 7. Mole concentration changes in a series of saddle azeotropes $[(-)(A, P), (+)H_2]$ $(+)H_i]$ as a function of boiling temperature of the non-polar component hydrocarbon H_i.

top-ridge line may, if the boiling temperature isobars for all of the binary systems are known, be determined with sufficient accuracy. Such a generalization may prove to be a first step towards further understanding of the phenomena under investigation. It is also possible to

calculate fairly accurately the boiling temperature depression of a ternary saddle azeotrope in comparison with the boiling temperature of a binary negative azeotrope [(−)(A,P)], if one considers the latter as one of the components and applies a correlation similar to that applied by Lecat [9], or recently by Malesiński [7] with regard to a series of binary azeotropes. For this purpose, it seems to be reasonable to use an equation in which the square root of the value of azeotropic depression is a function of the boiling temperature of the non-polar component H_i.

5. Concluding remarks

In a series of saddle azeotropes formed by a non-polar component (hydrocarbon), a weak acid (acetic acid) and a weak base (pyridine), there appear certain regularities, which enable an interpolation of the compositions and the boiling temperatures of azeotropes formed by corresponding paraffinic hydrocarbons. It is worthy of note that the projection of the top-ridge line is slightly shifted from the main line towards the "pyridine" side of the concentration triangle. This may be explained by the fact that the azeotropic range of pyridine $Z_p(H_i)$ is smaller than that of the acetic acid $Z_A(H_1)$ in relation to a series H of corresponding hydrocarbons. This means that the boiling temperature isobars in binary systems of acetic acid and hydrocarbons are characterized by minima on the corresponding isobars lying much lower in comparison with the boiling temperatures of corresponding mixtures of pyridine and hydrocarbons. Hence, a greater convexity appears on the tridimensional surface of the boiling temperature isobars in the part adjacent to the side AH_i. This favours the shifting of the top-ridge line towards the PH_i side. Further details concerning this matter will be published elsewhere. It should be emphasized that the top-ridge line projection is always shifted from the main line towards the greater content of that azeotropic agent which has a lower azeotropic range in relation to a series H. Some exceptions seem to exist in instances in which $t_{H_i} > t_A > t_P$.

I am greatly indebted to Prof. W. Świętosławski for enabling me to carry out these experiments, as well as for his valuable advice. I wish to express my thanks also to Mrs M. Zięborakowa and T. Drozdowska, W. Brzostowski and A. Turski for experimentally investigating individual ternary systems.

Summary

1. An investigation was made of a series of positive-negative (saddle) azeotropes formed by acetic and pyridine with paraffins: *n*-heptane, *n*-octane, *n*-nonane and *n*-decane.

2. A geometrical generalization was given, establishing the correlation between the compositions of the binary positive pairs of azeotropes and the saddle ternary azeotrope.

3. It was established that the shape of the tridimensional surface of the boiling temperature isobars in positive – negative systems, as well as that of the top-ridge line or its projection, depends on the values of the azeotropic ranges of the weak acid and the weak base in relation to a series of non-polar substances, e. g. hydrocarbons.

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CHEMISTRY

The Chemistry of Carbonyl Cyanide. I. The Reaction between Carbonyl Cyanide and α-Methylstyrene or Allylbenzene

by

O. ACHMATOWICZ, M. LEPLAWY and A. ZAMOJSKI

Presented by O. ACHMATOWICZ on August 22, 1955

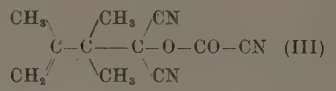
Despite its simple composition, carbonyl cyanide was unknown until comparatively recently. It was first obtained in 1937 by Małachowski and Jurkiewicz [1], and little is known of its chemistry. Actually, all relevant data are contained in four papers by Małachowski and his co-workers [1], [2], [3], [4]. The following are the main points of these papers: carbonyl cyanide, a slightly yellow, low boiling liquid, is comparable in reactivity to phosgene. It is explosively decomposed by water, reacts vigorously with simple alcohols, and readily combines with primary and secondary amines, to give derivatives of cyanoformic acid.

Carbonyl cyanide is not a specific reagent for the double bond. It reacted only with olefines containing $\cdot\dot{C}H-\dot{C}=\dot{C}\cdot$ grouping. The reaction proceeded without a catalyst and the highest reactivity was exhibited when both carbons of the ethylenic linkage were quaternary.

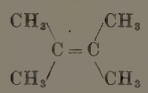
It should be emphasised that Małachowski's conclusions were chiefly based on qualitative tests. Only two hydrocarbons were examined in greater detail: tetramethylethylene (I) and cyclohexene (II). It was found that the reaction with either of the olefines inescapably involved two mols of carbonyl cyanide and proceeded according to equation (1)

$$C_nH_{2n}+2CO(CN)_2=C_nH_{2n-1}C_5O_2N_2+HCN. \tag{1}$$

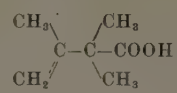
For the products obtained from tetramethylethylene or cyclohexene, two analogous pairs of alternative structures were proposed. The first pair, (III) and (IV), accounted for the formation of dimethylisopropenylacetic acid (V) [5], [6] on hydrolysis of the product derived from tetra methylethylene:



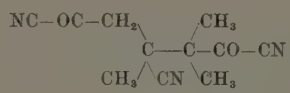
(III)



(I)

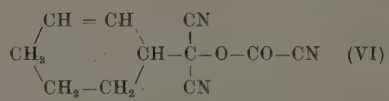


(V)

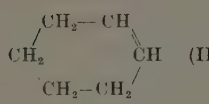


(IV)

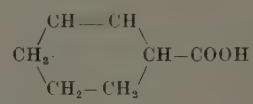
The second pair, (VI) and (VII), accounted for an analogous formation of Δ-2-cyclohexenecarboxylic acid (VIII) [7] from the product derived from cyclohexene.



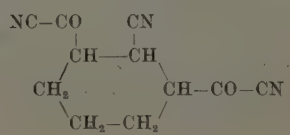
(VI)



(II)



(VIII)



(VII)

In experiments carried out in our laboratories we examined the action of carbonyl cyanide on the following unsaturated hydrocarbons:

a.

$Ph-CH=CH-CH_3$
$Ph-CH=C(CH_3)_2$
$Ph-C(C(CH_3)_3)=CH_2$
$Ph_2C=C(CH_3)_2$
$Ph_2C=CH-CH_3$
$Ph-CH=CH-CH=CH-Ph$
$Ph_2C=CH-CH=CPh_2$

b.

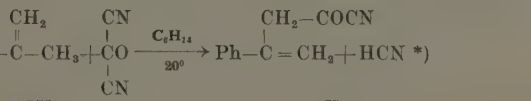
$Ph-C(CH_3)=CH_2$
$Ph-CH_2-CH=CH_2$
$p-CH_3-C_6H_4-C(p-CH_3-C_6H_4)=CH_2$
$CH_2=C(CH_3)-C(CH_3)=CH_2$
$Ph_2C=CH_2$

The reagent was found to be inactive towards the olefines of column "a", and those of column "b" were attacked by it in the cold without a catalyst.

These observations qualify Małachowski's rule. For instance, both carbons of the double bond of dimethyldiphenylethylene are quaternary and, according to the rule, the hydrocarbon should react readily with carbonyl cyanide, while in fact it was inactive. On the other hand, diphenylethylene has no hydrogen at the allylic position; nevertheless, contrary to the rule, it reacted vigorously with carbonyl cyanide.

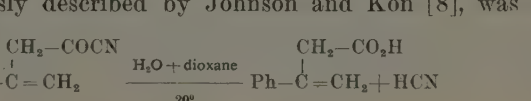
As mentioned, Małachowski found it impossible to make cyclohexene and tetramethylethylene react with only one mol of carbonyl cyanide. This, of course, seriously obstructed the elucidation of the mechanism of the reaction. We succeeded in overcoming this difficulty by fortunately choosing α-methylstyrene (IX) as one of the first objects of our investigations. This hydrocarbon turned out to be capable of reacting with one as well as with two mols of carbonyl cyanide.

Reaction with one mol of carbonyl cyanide. The reaction was conducted in hexane solution at room temperature. Hydrogen cyanide was evolved, and the oily product was recognised as β-phenylvinylacetyl cyanide (X).

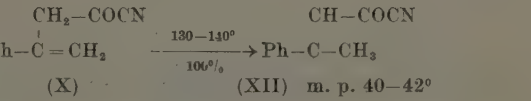
(2)


Evidence was supplied by the following experiments:

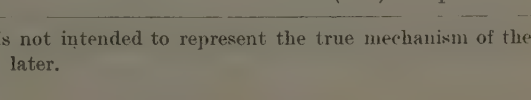
(i) When the oily product (X) was hydrolysed by cold water in dioxane solution, hydrogen cyanide was evolved and β-phenylvinylacetic acid (XI), previously described by Johnson and Kon [8], was formed:

(3)


(ii) After heating to 130°, the oily product (X) isomerised to a crystalline substance, m. p. 40—42°. It was assumed to be β-methylcinnamyl cyanide (XII).

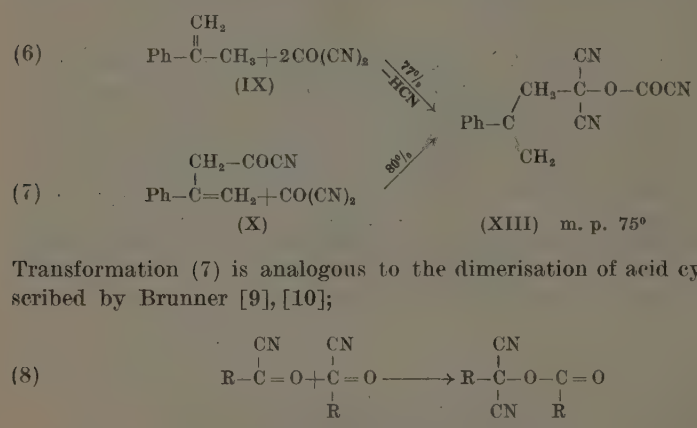
(4)


This was actually confirmed by the following synthesis:

(5)


*) Equation (2) is not intended to represent the true mechanism of the reaction. This will be discussed later.

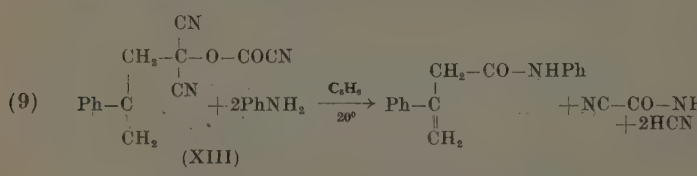
Reaction with two mols of carbonyl cyanide. Combination occurred at room temperature (equation (6)), again with evolution of hydrogen cyanide — and the crystalline product $C_{14}H_9O_2N_3$, m. p. 76.5°; resulted. The same compound was formed by treating (X) with carbonyl cyanide. We established that this compound has constitution (XIII) and was probably formed by addition of carbonyl cyanide to the carbonyl group of (X) (equation 7).



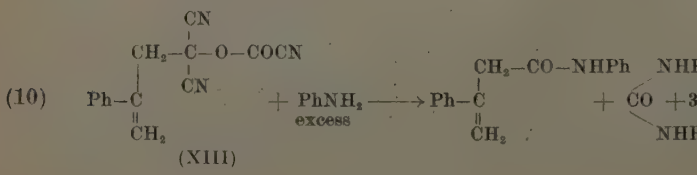
Transformation (7) is analogous to the dimerisation of acid cyanides, described by Brunner [9], [10];

Below are given the experimental facts which justify the assumed structure of product (XIII).

(i) When (XIII) was allowed to react at room temperature with exactly two mols of aniline in benzene solution β-phenylvinylacetanilide, cyanoformanilide and hydrogen cyanide were formed:



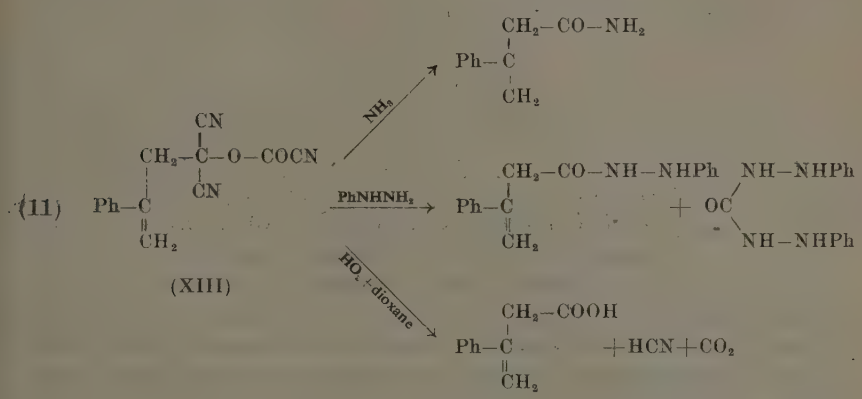
(ii) When aniline was used in excess, the same products were obtained, with the exception of cyanoformanilide in the place of which diphenylurea was produced:



(iii) With 10% ammonia, β-phenylvinylacetamide was obtained (equation (11)).

(iv) With excess of phenylhydrazine, the corresponding hydrazide together with 1.5-diphenylcarbohydrazide were produced (equation (11)).

(v) Hydrolysis with water in dioxane solution at room temperature yielded free β-phenylvinylacetic acid (equation (11)):



The second hydrocarbon examined was allylbenzene *). Unlike α-methylstyrene, it could not be made to react with a single mol of carbonyl cyanide. Invariably, two mols of the reagent were involved. The reaction, performed at room temperature in hexane solution, proceeded with evolution of hydrogen cyanide, furnishing the crystalline substance, $C_{14}H_9O_2N_3$, m. p. 106—111°. The composition of the product suggested that it was formed as shown in equation (12) and that it has constitution (XIV), analogous to that of the compound (XIII) obtained from α-methylstyrene and two mols of carbonyl cyanide:

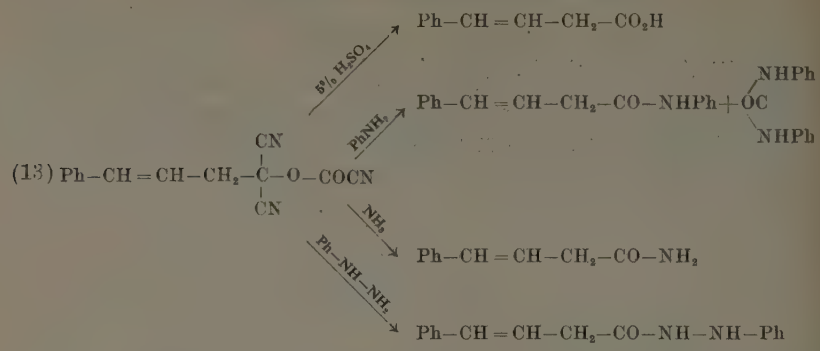
$$\text{(12)}\quad Ph{-}CH_2{-}CH{=}CH_2 + 2CO(CN)_2 \xrightarrow[\substack{20^\circ \\ 72\%}]{C_6H_{14}} Ph{-}CH{=}CH{-}CH_2{-}\overset{\overset{CN}{|}}{\underset{\underset{CN}{|}}{C}}{-}O{-}CO{-}CN + HCN$$

(XIV) m. p. 106—111°

Degradation experiments proved this to be correct.

As in the preceding case, the product was subjected at room temperature to the action of aniline, phenylhydrazine, ammonia and was hydrolysed with 5% sulphuric acid. The results are summarised in equation (13).

*) The experiments were performed in part by H. Lifszyc.

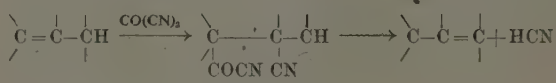


This shows that the product discussed was a derivative of styrylacetic acid thus implying that, during the reaction of allylbenzene with carbonyl cyanide, migration of the double bound occurred.

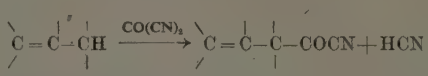
Some light is thus shed on the mechanism of the reaction between carbonyl cyanide and olefines. Since the second stage of the reaction between α-methylstyrene or allylbenzene and two mols of carbonyl cyanide has been explained, we shall now consider the mechanism of the first stage, i. e., the reaction between the olefines and the first mol of carbonyl cyanide.

Two possibilities could be advanced:

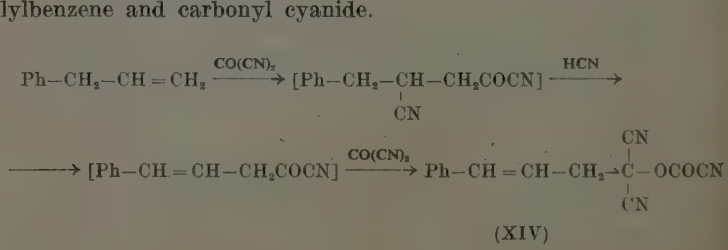
A. Addition of carbonyl cyanide to the double bond followed by elimination of hydrogen cyanide:



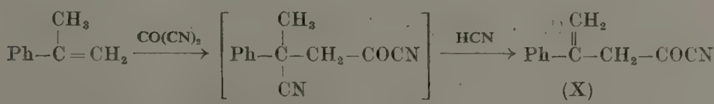
B. Substitution at the allylic position:



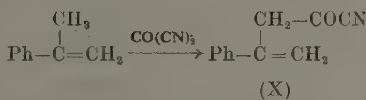
Elimination substitution would account for the formation of (XIV) from allylbenzene and carbonyl cyanide.



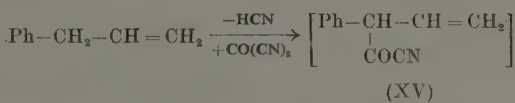
But this fails to explain the production of β-phenylvinylacetyl cyanide (X) from α-methylstyrene and carbonyl cyanide. The argument is, that the pertinent equation (17) is contrary to Saytzeff's rule and violates the principle of maximum conjugation:

(17) 

With allylic substitution, the situation is reversed. Thus we get a formally plausible explanation for the formation of β-phenylvinylacetyl cyanide (X):

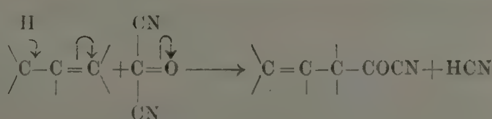
(18) 

But for the reaction of allylbenzene with carbonyl cyanide (equation (19)) this mechanism cannot be accepted, since its predictions (formation of (XV)) are at variance with experiment.

(19) 

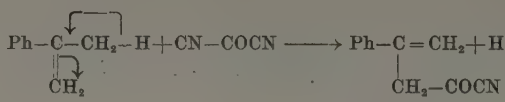
These discrepancies undermine the validity of both the concepts. However, the difficulty of embracing the reaction discussed by a uniform explanation may be overcome, if hyperconjugation is taken into account.

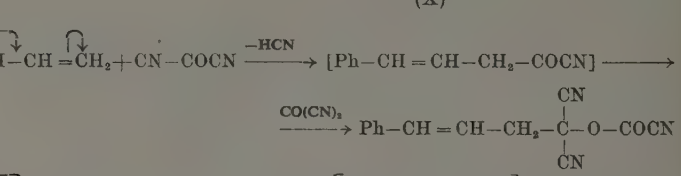
On this hypothesis, it is now proposed (A. Zamojski) to represent the reaction of carbonyl cyanide with α-methylstyrene or allylbenzene by the general equation (20).

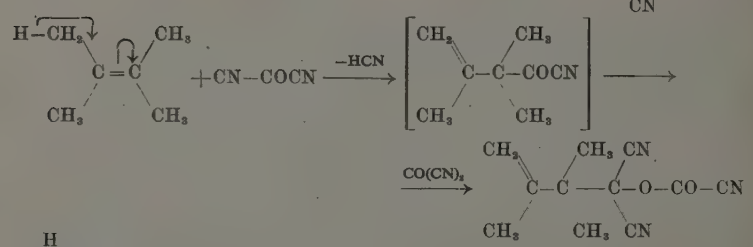
(20) 

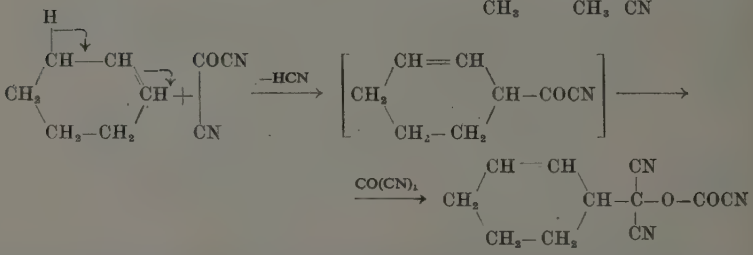
Predictions implied by this mechanism, which might be termed "1.3-addition-elimination", are in perfect harmony with experimental data in the cases not only of α-methylstyrene and allylbenzene, but also of tetramethylethylene and cyclohexane.

This is seen from equations (21), (22), (23) and (24), which hardly need to be discussed.

(21)


(22)


(23)


(24)


Further experiments on the mechanism for the reaction of carbonyl cyanide with olefines containing hyperconjugated systems are in progress.

One of us (O.A.) wishes to express his thanks to Dr. J. W. Baker of the University of Leeds for a discussion.

This paper was presented at the XIV-International Congress of Pure and Applied Chemistry in Zurich in July 1955.

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POLONAISE DES SCIENCES
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CHEMISTRY

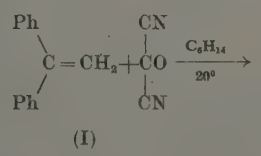
The Chemistry of Carbonyl Cyanide. II. The Action of Carbonyl Cyanide on 1,1-Diphenylethylene. Formation of a Compound Believed to be a Cyclopropane Derivative

by

O. ACHMATOWICZ and M. LEPLAWY

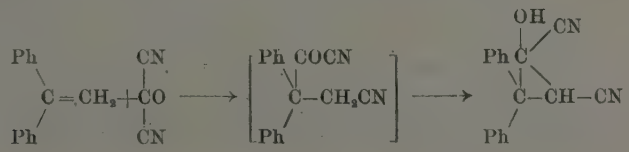
Presented by O. ACHMATOWICZ on August 22, 1955

In Part I (preceding paper) it was suggested that the reaction between carbonyl cyanide and certain olefines containing the $\cdot\dot{C}H-\dot{C}=\dot{C}\cdot$ grouping has in its first stage a mechanism dependent on the presence of a hyperconjugated system and was termed "1.3-addition-elimination". It is now found that the presence of a hydrogen atom at the allylic position is not necessary for an olefine to react with carbonyl cyanide but, in this case, the mechanism of the reaction is different. This conclusion was arrived at on examining the behaviour of carbonyl cyanide towards 1,1-diphenylethylene (I). The experiments were conducted at room temperature in hexane solution and yielded the following products:

(1) 

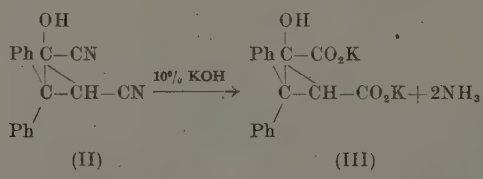
A. (II) $C_{17}H_{12}ON_2$ m. p. 108° (> 60%);
B. $C_{30}H_{22}N_2$ m. p. 137° (10%);
C. $C_{28}H_{24}$ m. p. 72° (<3%);
resin (>20%); gases (HCN)

Only the main product A will be discussed. It had a composition corresponding to an addition product of carbonyl cyanide to diphenylethylene, but subsequent investigations indicated that it is rather a cyclopropanol derivative of structure (II) and that it was formed from the intermediate "a" by internal aldol condensation:

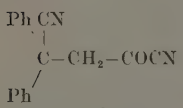
(2) 

Structure (II) was advanced on the basis of the following experiments. When A (II) was hydrolysed by aqueous 10% potassium hydroxide, two mols of ammonia were formed and a potassium salt (III) of a dibasic acid $C_{17}H_{14}O_5$ was obtained (yield 85%):

(3)



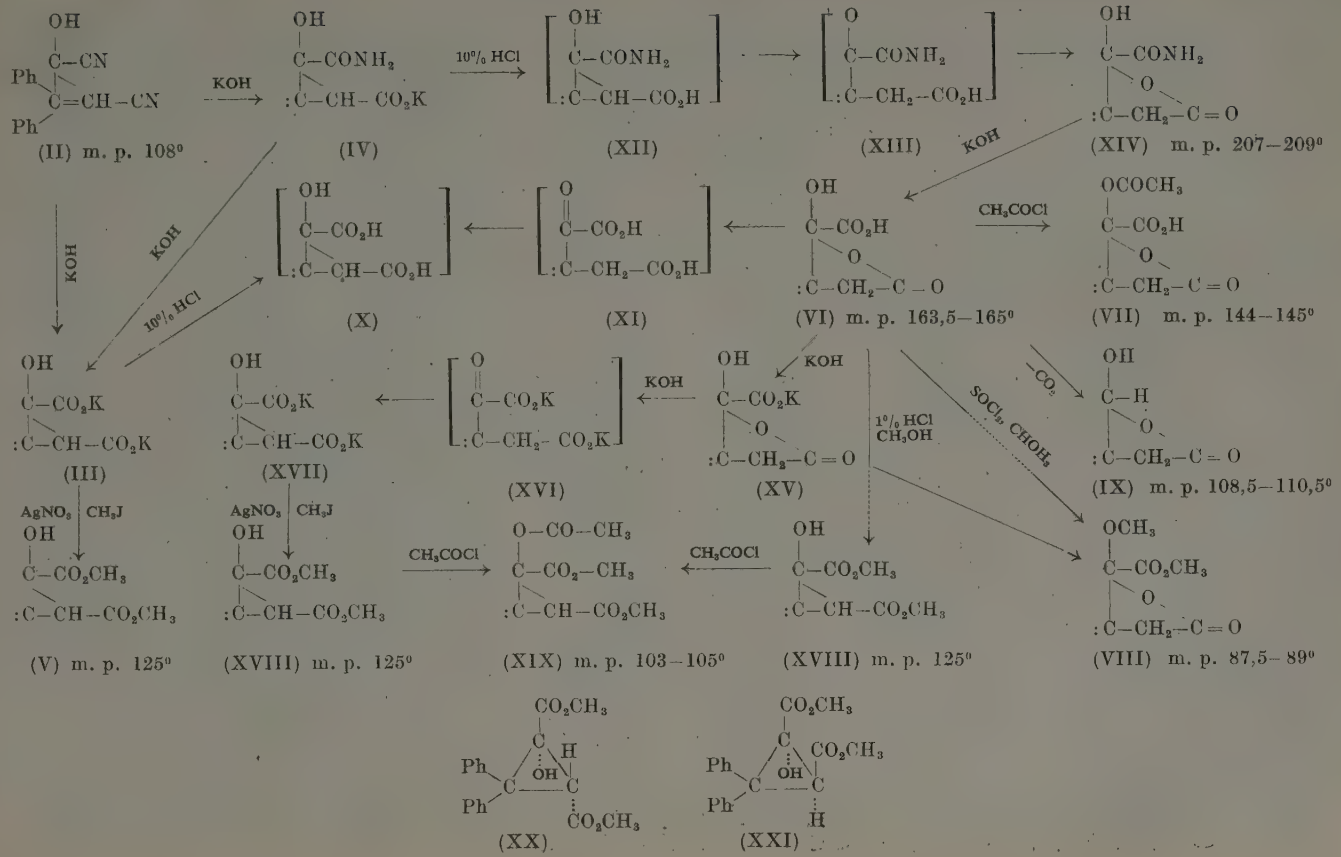
The formation of two mols of ammonia revealed that A (II) contained no COCN residue, but was undoubtedly a dinitrile. It is also evident that the intermediate in equation (2) could not have structure "b" since a compound of such constitution would yield, on hydrolysis, one mol each of ammonia and hydrogen cyanide, and would be incapable of the assumed internal aldol condensation. Hydrolysed under more gentle conditions with potassium hydroxide, A (II) yielded a monoamide (IV) which, on further hydrolysis by the same reagent (Chart), gave (III). (III) was converted into the corresponding silver salt $C_{17}H_{12}O_5Ag_2$ and that, on being digested with methyl iodide, furnished a dimethyl ester $C_{19}H_{18}O_5$ (V) m. p. 125—127°.



b.

When (III) was acidified in order to liberate the corresponding acid, an oily precipitate was formed which crystallised after several hours. However, contrary to expectation, the substance proved to be not a dibasic but an isomeric monobasic acid $C_{17}H_{14}O_5$ m. p. 163.5—165°. It is assumed to be a lactol of constitution (VI). This view was supported by the following evidence.

(VI) readily reacted with acetyl chloride, yielding an acetate $C_{19}H_{16}O_6$ (VII) m. p. 144—145°. When (VI) was treated in dry state with thionyl chloride and, the reaction completed, gently warmed with methyl alcohol, it was quantitatively converted into a dimethyl derivative $C_{19}H_{18}O_5$ (VIII), m. p. 87.5—89°. (VIII) was also formed in moderate yield, when (VI) was methylated in the cold by 1% methanolic solution of hydrogen chloride. When (VI) was cautiously heated slightly above melting point, carbon dioxide was split off and a crystalline compound $C_{16}H_{14}O_3$, m. p. 108.5—110.5°, believed to have structure (IX), was produced. It was insoluble in sodium carbonate but slowly dissolved in sodium hydroxide, yielding a solution which reduced the Tollens reagent, in conformity with the advanced formula (IX). Compound (IX) was able to be recovered unchanged from alkaline solution by acidification with hydrochloric acid followed by gentle warming.


(II) m. p. 108°
KOH
(IV)
10% HCl
(XII)
(XIII)
KOH
(XIV) m. p. 207–209°
KOH
10% HCl
(X)
(XI)
(VI) m. p. 163,5–165°
CH₃COCl
(VII) m. p. 144–145°
(III)
(XVII)
(XVI)
KOH
(XV)
1% HCl
CH₃OH
SOCl₂, CHOH₃
–CO₂
(IX) m. p. 108,5–110,5°
AgNO₃
CH₃J
(V) m. p. 125°
(XVIII) m. p. 125°
CH₃COCl
(XIX) m. p. 103–105°
(XVIII) m. p. 125°
(VIII) m. p. 87,5–89°
(XX)
(XXI)

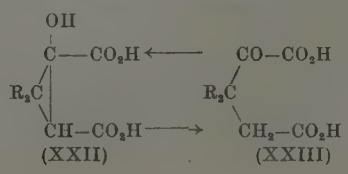
The evidence so far presented suggests that the conversion of (III) into (VI), under the action of an acidic medium, is a cyclol-lactol transformation proceeding through intermediate stages (X) and (XI).

A quite similar transformation was assumed to occur when amide (IV) was acidified with dilute hydrochloric acid in the cold. It was thus converted into a lactolic amide $C_{17}H_{15}O_4N$ (XIV) m. p. 207—209° from which lactol (VI) was obtained by gentle warming with dilute alkali, followed by acidification. When (VI) was neutralised with dilute potassium hydroxide, the corresponding salt (XV) was obtained. When, however, (VI) as well as (XV) were gently heated (or kept for several days) in alkaline solution, a reverse change, i. e., lactol→cyclol, took place and a potassium salt of a dibasic acid $C_{17}H_{14}O_5$ (XVII) was formed. (XVII) was converted into the corresponding silver salt $C_{17}H_{12}O_5Ag_2$ which, heated with methyl iodide, gave the dimethyl ester $C_{19}H_{18}O_5$ (XVIII), m. p. 124.5—125.5°. The latter was also obtained, as a main product (along with the dimethyl derivative (VIII) already discussed), when (VI) was acted upon by a cold 1% methanolic solution of hydrochloric acid. The formation of (VIII) and (XVIII) in the latter reaction is explained if we assume that lactol (VI), on being dissolved in 1% methanolic solution of hydrogen chloride is partly transformed, for instance via (XI), into the cyclol (X).

Dimethyl esters (V) and (XVIII) had the same composition and both melted at 124.5—125.5°. However, these compounds were not identical, as was shown by the large depression of the mixed melting point. It was found that the isomer (XVIII) readily reacted with acetyl chloride, yielding an acetate $C_{21}H_{20}O_6$ (XIX), m. p. 103—105°, whereas the isomeride (V) failed to undergo acetylation. Those results suggested that (V) and (XVIII) are stereoisomers and have configurations cis and trans respectively, as shown by the relative formulae (XX) and (XXI).

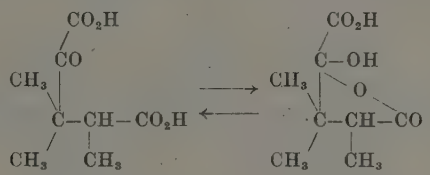
If the chemical behaviour of cyclol (X) and lactol (VI) is compared with that of analogous compounds described in literature, it may be concluded that the former two substances represent exceptional cases as regards their great tendency to internal transformation. To make this point clear, it may be profitable to recall briefly the work done on the subject by Thorpe and his school [1].

They showed that spiro-cyclopropanoldicarboxylic acids (XXII) fail to isomerise into the corresponding open-chain α-ketoacids (XXIII). The ability to isomerise, is however, exhibited by disubstituted cyclopropanoldicarboxylic acids, when R_2 stands for Et_2 or Pr_2.



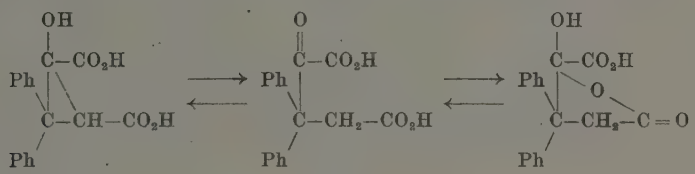
As to open-chain α-ketodicarboxylic acids (XXIII), these have been found by British chemists to be incapable of rearranging into the corresponding cyclopropanoldicarboxylic acids. This was established for α-ketoglutaric acid itself and for its gem-disubstituted analogues, when R_2 stood for H_2, Me_2 or spirocyclopentyl.

In only one instance was conversion of an open-chain α-ketodicarboxylic acid to the corresponding lactol described. This was the case of the Balbiano acid which, according to Thorpe and his co-workers, has structure (XXV) when in crystalline state, and in solution partly transforms into (XXIV).



(XXIV) (XXV)

Cyclol (X) and lactol (VI) represent interesting cases not only because of their ready liability to reversible ring opening and closure but mainly because their interconversion embraces a wider range of structures:



(X) (XI) (VI)

It is perhaps too soon to offer an explanation of this phenomenon, but there is a suggestion that an important rôle is played in the compounds discussed by the two aromatic systems in gem-position.

Reverting to the reaction between diphenylethylene and carbonyl cyanide, it seems, from the entire evidence so far presented, that substance (II) in fact has the proposed structure. If so, then the first stage of the reaction between diphenylethylene and carbonyl cyanide must be, as at first proposed, a normal addition to the double bond.

It is evident that further research should be done over the complete elucidation of the precise mechanism of the reaction between olefines and carbonyl cyanide. Nevertheless, hitherto existing data presented in both this and the preceding papers, permit the assumption that olefines in which hyperconjugation exists react — if at all — with two mols of carbonyl cyanide according to the 1.3-addition-elimination mechanism followed by Brunner's "co-dimerisation", while in the absence of hyper-

conjugation, one mol of the reagent is involved and the reaction — if any — is in its first stage merely a normal addition to the ethylenic linkage.

One of us (O.A.) wishes to express his thanks to Professor C. K. Ingold, F.R.S. for a discussion.

This paper was presented at the XIV-International Congress of Pure and Applied Chemistry in Zurich in July 1955.

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BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Cl. III — Vol. III, No. 10, 1955

CHEMISTRY

The Alkaloids of *Lycopodium Selago* L.

by

O. ACHMATOWICZ and W. RODEWALD

Presented by O. ACHMATOWICZ on August 22, 1955

The "crude alkaloid" of *Lycopodium selago*, designated selagine, was first described by Muszyński [1], who claimed that it was identical with the alkaloid pillijanine isolated by Arata and Canzoneri [2] from the South American *Lycopodium saururus*. The assumption was chiefly based on pharmacological experiments which revealed that, unlike alkaloids of other European Lycopodium species, both substances possessed the property of contracting the pupil and reducing the intraocular pressure. This activity of selagine was confirmed by the clinical observations of Miratyńska-Ernestowa [3] who showed that the alkaloid may be used as a substitute for pilocarpine or eserine in treatment of *glaucoma chronicum acutum secundarium*.

A chemical analysis of the "crude alkaloid" of *L. selago* (collected July–August in Podkarpacie, Poland) has shown that it contains at least four crystalline alkaloids. They were isolated only after a laborious fractional crystallisation of the perchlorate or the hydriodide of the "crude alkaloid". These alkaloids were:

1) lycopodine, described by Achmatowicz and Uzięblo [4], as the chief alkaloidal constituent of *L. clavatum*;

2) acrifoline, isolated by Bertho and Stoll [5] from *L. annotinum* of German origin;

3) alkaloid L8, previously found by Manske and Marion [6] to occur in *L. annotinum* of Canadian origin; and

4) an isomeride of clavatine [4] ($C_{16}H_{25}O_2N$), which is either a new substance or identical with alkaloid L23, isolated by Manske and Marion [7] from *L. lucidulum Michx.* This alkaloid has been designated as pseudoselagine.

The percentage of alkaloids contained in dry plant of *L. selago* is recorded in Table I.

TABLE I

Alkaloid content of *Lycopodium selago* L.
(4 kg. of plant matter. cont. 16% H_2O)

	%% in reference to		g
	dehydrated mat.	total amount of crystal. alkal.	
Crude alkaloid	0.164		5.5
Crystalline alkaloids	0.072		2.42
Lycopodine	0.053	74.4	1.8
Pseudoselagine	0.015	20.7	0.5
Acrifoline	0.002	3.1	0.075
Alkaloid L8	0.001	1.8	0.045
Oily fraction	0.092		2.9

Pseudoselagine possesses basic properties; it is soluble in dilute acids, and is precipitated therefrom by excess of ammonia or alkalis. It is bitter to the taste and laevorotatory ($[\alpha]_D^{19} = -42.7^0$). Solutions of pseudoselagine in dilute hydrochloric acid form precipitates with the usual precipitants for alkaloids. The base gives colour reactions also. Pseudoselagine crystallises from acetone in sick plates, m. p. 163°. It contains neither OMe nor NMe, and OH and NH groups are also absent. It is not hydrogenated in presence of palladinised charcoal and is indifferent towards reagents for the carbonyl group. It is not attacked by boiling ethanolic potassium hydroxide. It forms a hydrochloride, m. p. 307°; a hydriodide, m. p. 314°; a perchlorate, m. p. 295°. It also forms a methiodide, m. p. 279°, and a methochloride, m. p. 268°, both these derivatives exhibiting the properties of quaternary ammonium salts.

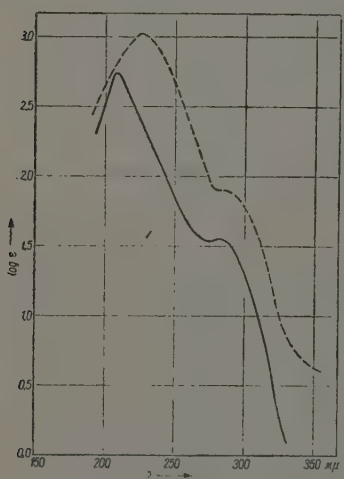

Fig. 1. The ultraviolet light-absorption pseudoselagine m/25 ——— alkaloid L8 m/100 – – – in 96% ethanol.

The ultraviolet light-absorption spectra of pseudoselagine and alkaloid L8 have been determined and the relevant curves are recorded in the diagram.

The pharmacological activity of pseudoselagine and acrifoline as well as that of annotinine, isolycopodine and alkaloid L11, previously found by Achmatowicz and Rodewald [8] to occur in *L. annotinum* of

Polish origin, were kindly examined by Professor Kubikowski and his co-workers of Warsaw University. The toxicity of these alkaloids (Korber's method, white mice) was found to be as follows:

TABLE II

Toxicity of certain *Lycopodium* alkaloids

Name	LD_{50}
Annotinine	6.49 mg./100 g. mouse
Acrifoline	7.06 „ „
Isolycopodine	8.16 „ „
Alkaloid L11	17.90 „ „
Pseudoselagine	6.26 „ „

None of the alkaloids exhibited the property of contracting the pupil. Nor did they haemolize red cells (in rabbits) or cause irritation of the mucosa.

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[7] — Can. J. Res., **24** (1946), 57.
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BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Cl. III — Vol. III, No. 10, 1955

CHEMISTRY

The Application of Muconic Ester to Diene Additions

by

O. ACHMATOWICZ and J. WRÓBEL

Presented by O. ACHMATOWICZ on August 22, 1955

Muconic ester appears to be, among simple derivatives of butadiene, the only one not yet investigated in detail as a component in the Diels-Alder reaction. Actually, only maleic anhydride has been condensed with this ester. The result, as shown by Farmer and Warren [1] and confirmed by Alder and Vagt [2] was a normal adduct.

We thought it worth while to extend the study and to examine the reaction of muconic ester with other typical dienophiles leading to derivatives of tetrahydroterephthalic acid.

The experiments showed that muconic ester is a diene of somewhat low reactivity. In most cases, the reaction had to be carried out at 150°-160°, and was conducted in sealed tubes in xylene solution. The products, mainly oily liquids, were isolated by distillation in a high vacuum. The actual yields were below 60% — usually about 35% — of theoretical yields.

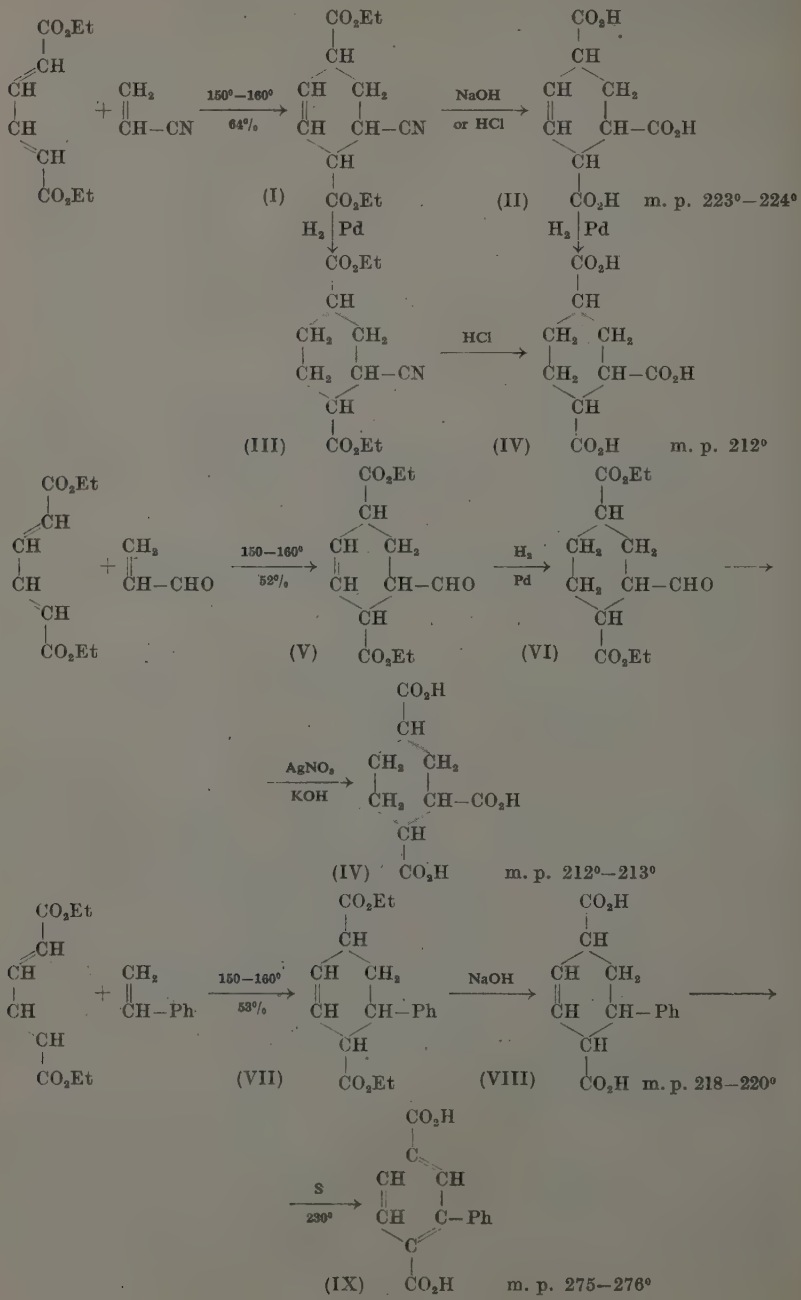
Of the nine dienophiles examined, six gave normal adducts, while the remaining three gave a more complicated reaction with muconic ester. The six were: vinyl cyanide, acrolein, dichloroethylene, styrene, acetylenedicarboxylic ester and diazoacetic ester. The remainder comprised allyl alcohol, nitroethylene and β-nitrostyrene.

The structure of the adduct (I) obtained from vinyl cyanide was established by conversion, as previously described by Goldsworthy and Perkin [3] into cyclohexanetricarboxylic acid (IV):

Our specimen was, as judged by its melting point (212°), a mixture of cis and trans isomerides.

It should be noted that the position of the double bond was not established in either adduct (I) or any of the other adducts to be discussed.

The same cyclohexanetricarboxylic acid (IV) was obtained from the aldehydic product (V) formed in the reaction of muconic ester with acrolein:


150°–160°
64%
NaOH
or HCl
(I)
(II)
m. p. 223°–224°
H_2 Pd
HCl
(III)
(IV)
m. p. 212°
150–160°
52%
H_2
Pd
(V)
(VI)
$AgNO_3$
KOH
(IV)
m. p. 212°–213°
150–160°
53%
NaOH
(VII)
(VIII)
m. p. 218–220°
S
230°
(IX)
m. p. 275–276°

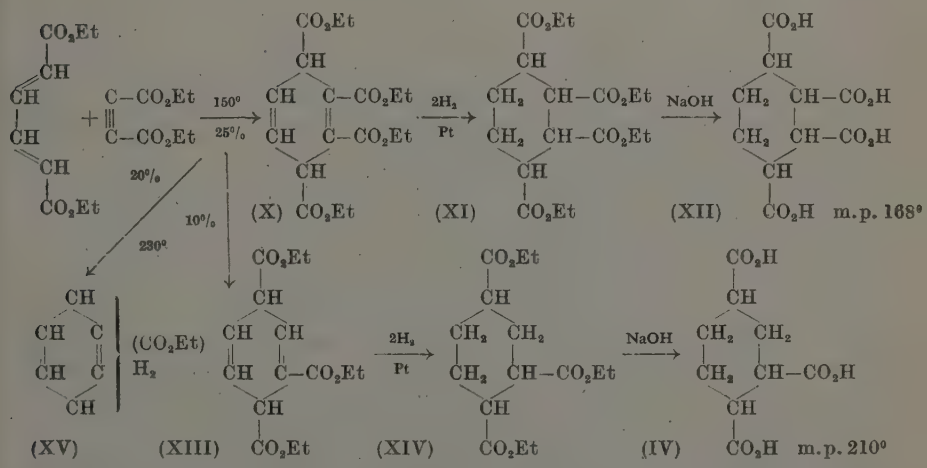
Aldehyde (V) and its dehydroderivative (VI) were characterised as dinitrophenylhydrazones (m. p. 104—105° and 117—119° respectively). The yield of stage (VI—IV) was poor.

The condensation product of styrene with muconic ester is also undoubtedly a normal adduct, although we have no direct evidence to prove that the suggested structure (VII) is correct:

On hydrolysis, adduct (VII) gave a dibasic acid (VIII) which underwent aromatisation, furnishing acid (IX) after several hours of heating with sulphur at about 230°.

The condensation of muconic ester with acetylenedicarboxylic acid conducted at 150° yielded two substances.

(i) One of these was recognised as a normal diene addition product having structure (X). It reacted with 2 mols of hydrogen, yielding an ester (XI) which on hydrolysis by alkali gave cyclohexanetetracarboxylic acid (XII) as described by Farmer and Warren [1] and Alder and Vagt [2].



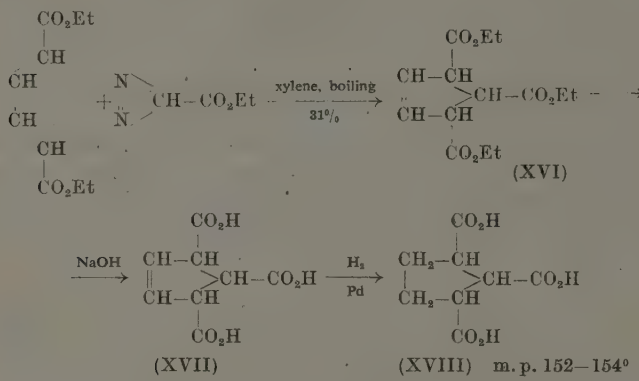
(ii) The second product was found to be an ester of a tricarboxylic acid and, as will become apparent, formula (XIII) should be ascribed to it. On being reduced on Adams catalyst, it took up 4 hydrogen atoms and the tetrahydroderivative (XIV) thus obtained gave Perkin's cyclohexanetricarboxylic acid (IV) on hydrolysis.

The formation of (XIII) in the diene addition discussed, would show that during the reaction a carboethoxy group is in some way split-off. Similar observations were quoted by Alder and Rickert [4] and Alder and Backendorf [5] from the condensation of acetylenedicarboxylic acid with butadiene.

We have found in addition that still another carboethoxy residue is lost when muconic ester is heated with acetylenedicarboxylic ester

at 230°–240°. The product had a composition corresponding to formula (XV), but the orientation of the carboethoxy groups has not yet been determined.

The reaction of muconic ester with diazoacetic ester proceeded, as could be predicted by analogy to diazometane [6], with evolution of nitrogen.



The structure (XVI) was confirmed by converting the product into cyclopentanetricarboxylic acid (XVIII) [7].

The condensation product of muconic ester with dichloroethylene was undoubtedly a normal adduct. We were unsuccessful in our attempt to obtain it in an analitycally pure state. Hydrolysed by alkali, it gave terephthalic acid. The overall yield was below 10%.

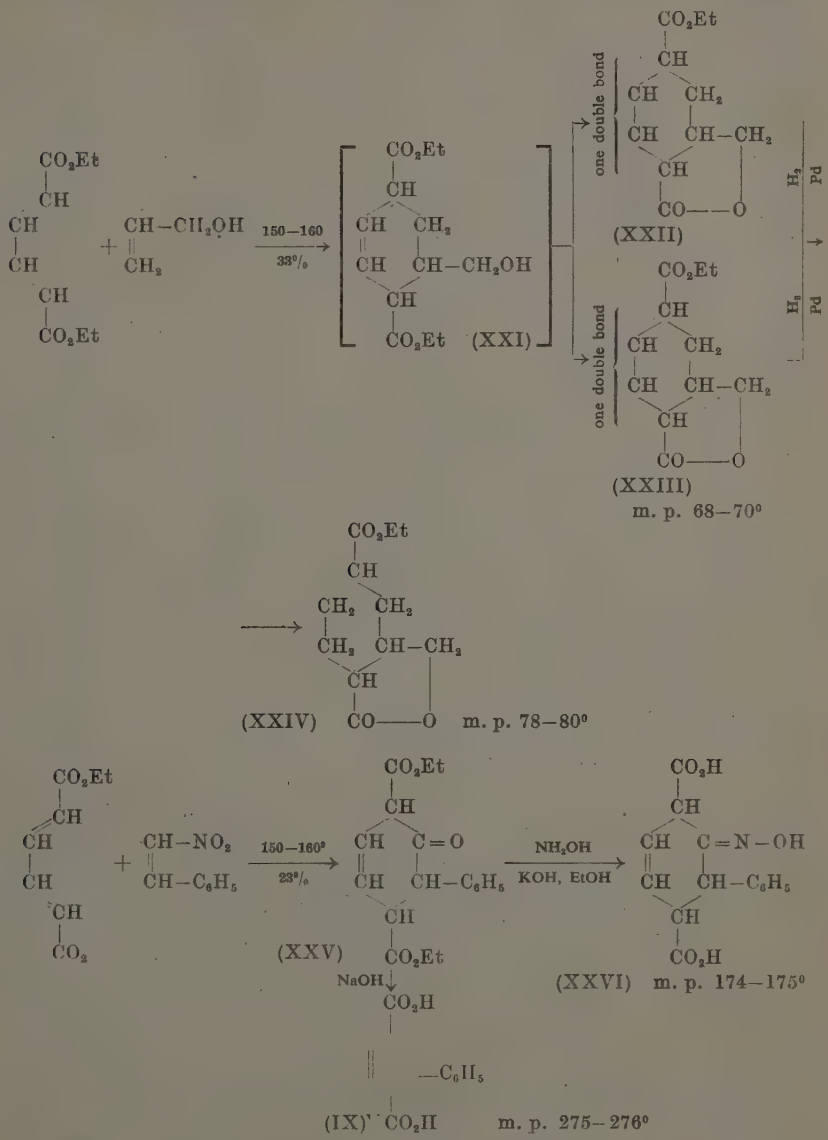
We now turned to condensations which gave unexpected results. In the first of these, allyl alcohol played the part of a dienophile. Two isomeric products resulted: one (XXII) was oily, and the other (XXIII), crystalline (m. p. 68–70°). Both yielded the same dihydroderivative, m. p. 78–80° (XXIV) on catalytic hydrogenation:

However, (XXII), (XXIII) as well as the dihydroderivative (XXIV) resisted acetylation and contained only one EtO-group each. These results suggested that all three are monoethylesters, the second carboxyl being incorporated in a lactonic system. This concept was also in conformity with molecular weight determinations, but all attempts to prove the lactonic structure by routine methods have so far been in vain.

An unusual result obtained in the reaction of β-nitrostyrene with muconic ester. It was established that the condensation proceeded with a steady evolution of nitrogen oxide:

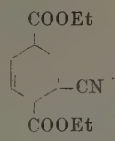
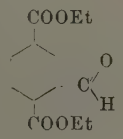
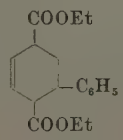
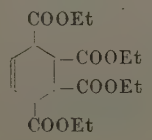
The product (XXV) contained no nitrogen and, on being digested in methanolic solution with hydroxylamine hydrochloride in the presence of kalium hydroxide, yielded an oxime, m. p. 174° of a ketodi-

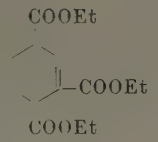
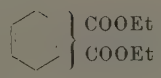
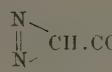
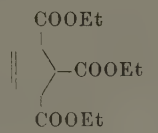
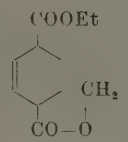
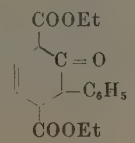
carboxylic acid. On the other hand, product (XXV) on being hydrolysed by 25% alkali furnished an acid which was identified with the phenyl-



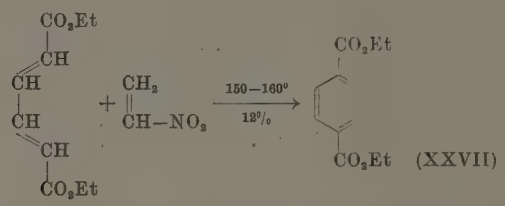
terephth alic acid (IX) already described. These experiments seems to justify formula (XXV) for the reaction product of β-nitrostyrene and muconic ester.

TABLE I

Dienofil	Adduct	Yield	b_p/m_p	d_4^{20}	n_D^{20}	MR	
						Calc.	Obs.
$CH_2=CH.CN$		64%	135–137°/0.01 mm.	1.1200	1.4739	62.79	62.90
$CH_2=CH.CHO$		52%	98–100°/0.01 mm.	1.1436	1.4814	63.07	63.1
$CH_2=CH.C_6H_5$		53%	94–98°/0.01 mm.	1.1260	1.5161	82.43	81.08
C.COOEt ‖ C.COOEt		25%	150–155°/0.01 mm.	1.1430	1.4815	88.82	91.8

		10%	130–135°/0.01 mm.	1.1440	1.4794	73.35	73.34
		20%	83°/0.001 mm.	1.0631	1.5680	58.18	60.33
		31%	92–94°/0.01 mm.	1.1110	1.4740	69.18	72.0
$CH_2=CH.CH_2OH$		33%	115–119°/0.01 mm.	1.1717	1.4860	51.63	51.5
$O_2N.CH=CH.C_6H_5$		23%	135°/0.01 mm.	1.1353	1.5085	82.75	82.99

Third and last of the dienophiles which behaved contrary to expectation was nitroethylene. Just like nitrostyrene, it gave with muconic ester a substance free of nitrogen, but here the change was evidently more drastic since the product proved to be the diethyl ester of terephthalic acid (XXVII):



(XXVII)

It should be noted that a similar course in diene addition was observed by Allen and Bell [8] in the case of tetracyclone and nitroethylene.

However, the mechanism of these reactions, still remains obscure.

Physical constants of some of the products described are recorded in Table I.

This paper was presented at the XIV-International Congress of Pure and Applied Chemistry in Zurich in July 1955.

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GEOLOGY

The Action of Rivers during the Glacial Epoch and the Stratigraphic Significance of Fossil Erosion Surfaces in Quaternary Deposits

by

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The problem considered is as follows:

To what extent did the climatic fluctuations of the Glacial Epoch — which found their expression in Glacial and Interglacial Phases — influence the change of the geomorphologic process in glaciated areas, or areas remaining under the influence of glaciation?

The problem involves, chiefly, the examination of river action. Numerous attempts have already been made to solve this key problem of the Quaternary Period.

It has been assumed, for instance, that alluvial sedimentation took place during the Glacials and that valley gravel-sheets were cut up in the Interglacials. The Glacial and Interglacial maxima (peaks of the climatic curve) were periods in which different morphogenetic processes took place [1], [2].

Another, more modern conception is that, from the morphological point of view, it is not the climate of the peak phases of the Glacials and Interglacials which is the most important, but the climatic changes between these extreme stages, i. e., sedimentation between the Interglacial and the Glacial Phases, and the erosion occurring between these Phases [3]—[5]. Trévisan [6] has called the first of these phases, the anaglacial, and the second — the kataglacial.

The author of the present paper wishes to submit, on the basis of the results of research work effected in the Lublin Plateau *), a new conception by way of explanation of this question.

*) A detailed proof of this thesis will be found in an extensive paper to appear in Prace Geograficzne Instytutu Geografii PAN (Geographical Treatises of the Polish Academy of Sciences Institute of Geography).

The stratification of quaternary deposits of the Lublin Plateau was determined, on the basis of numerous outcrops and boreholes. As a result of this investigation the morphological history of this area, from the Tertiary, through all the Glacial Periods, to the Holocene was examined.

It was established as a fundamental fact that each series of glacial and interglacial deposits is, as a rule, separated from the others by horizons of sedimentary incompatibility, — in other words, by surfaces of erosion or denudation. Each glacial series is dissected at the top. Interglacial deposits rest on these erosion surfaces. These phenomena appear, even though they cannot be established with complete certainty, in the deposit series of more ancient Glacial Phases; they become, on the other hand, increasingly evident in the deposits of the younger Pleistocene.

Such a development may be noted in the quaternary deposits which have been buried in the Pliocene Wieprz Valley (Fig. 1.).

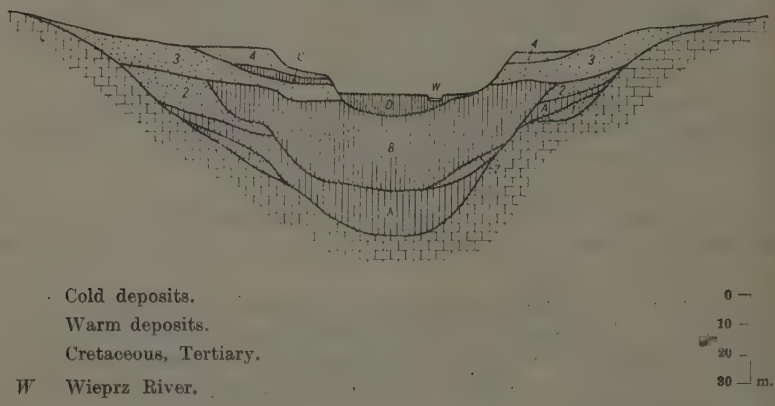

Fig. 1. Schematic section of the Wieprz valley, below the mouth of the Bystrzyca, drawn on the basis of material actually obtained from boreholes and excavations in the vicinity of the villages of Syrniki, Czerniejów, Rokitno and Spiczyn. The interposition of sedimentary cold series (moraine-tills, fluvioglacial, sands, boulders) between warm ones (fluvial sands, lake silts, peats) is clearly visible. The cold deposits (1, 2, 3, 4), originate from the Glacial, the warm ones (*A*, *B*, *C*, *D*) — from the Interglacial and Post--Glacial Phases. Between these are deep erosion surfaces, corresponding to the different stages of development of the Wieprz valley during the Quaternary Period.

This is shown, for example, in the section of the valley below the mouth of the Bystrzyca, a section which has been reconstituted on the basis of numerous profiles of the valley slope, and of boreholes on the valley bottom (according to Karaszewski [7]). The fossil erosion surfaces separate "cold" deposits (moraine-till, fluvioglacial sand) from "warm" deposits (fluvial sands, lake deposits and peat).

In the Wieprz valley, south of Krasnystaw, the cold deposits with a Dryas-flora (silt, clay and sand) rest on a deep erosion form, and are also dissected at the top by a similar surface.

The position is reversed in the valleys of the Bug and of the Huczwa, where a fossil erosion valley is buried beneath a thick series of warm deposits (with a paludina fauna). The fossil valley was cut in the deposits of the older Pleistocene.

This stratigraphic regularity can be clearly traced from the deposits of the last glaciation up to contemporary times. It is a branch of the climatic curve of the glaciation — if Trévisan's definition of the kataglacial phase is accepted. The principal fluviatile terrace in the valleys of the Lublin Plateau, was formed in the periglacial zone of the last glaciation. It is dissected to a depth of approximately 20 to 30 metres. Into this form, warm Holocene sediments, i. e., sediments of an interglacial type, are deposited. (Fig. 1).

From this data it may be concluded that sedimentation in river valleys took place both during the Glacial Phases (cold sedimentation) and the Interglacial Phases (warm sedimentation). In between those there were always erosion phases which may be called, according to Trévisan's terminology, the phases of anaglacial (before glaciation) and kataglacial (after glaciation) erosion.

It will be possible to locate these phases more accurately in the climatic curve by taking into consideration the changes in temperature and precipitations. Klute [8] once stated that these two curves were parallel one to the other, i. e., that the fall in the air temperature during the glaciation produced a proportionate fall in the volume of precipitations. It would appear, however, that this is not the case. The curves tend to intersect. During the Interglacial Phases, the total of precipitations was less than the thermal capacity of those periods, and above this limit during the Glacial Phases. It is a consequence of this fact that glacial cooling produced a marked, brisk exchange of air masses, and the edge of the icecap was a zone of cyclones.

The erosive action of flowing waters coincided, during the period of change of the Glacial climatic system, with the Interglacial Phases and vice versa. The Interglacial system itself was not conducive to any major degradation, against which the compact vegetation (forest) gave full protection. Neither did the glacial (periglacial) system admit, in spite of a lack of vegetation, of any deeper river cuttings, for the subsoil was frozen and the action of valley waters too weak. They were charged with material produced by the denudation — very intense at that period — of slopes. The period of passage from one system to another — shown by the intersection of the temperature and precipitation curves — produced conditions conducive to erosive action. Hence, it is from that

period that the erosion surfaces, known among the quaternary deposits of the Lublin Upland, originate.

The results of these considerations are summarised in the diagram (Fig. 2), which shows the course of the temperature and of precipitations during the Glacial and Interglacial Phases. It may be seen that the erosion phases, dividing the Interglacial from the Glacial (E_a), and the Glacial from the Interglacial (E_k), indicate the limits between the cycles of warm and cold sedimentation. Each cycle is composed of two parts, which – enlarging on Trévisan's [6] concepts – may be called

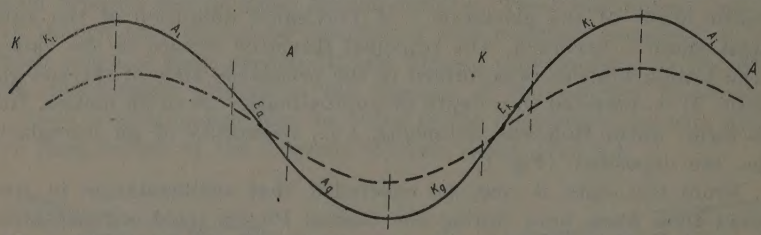

Fig. 2. The erosion and accumulation cycle of fluvial action in the Pleistocene. ——— temperature. – – – precipitations. A – anaglacial phase. K – kataglacial phase. E – erosion.

the anaglacial and kataglacial parts. The turning point of each cycle is equivalent to a climatic culmination or depression. Thus, each Interglacial Phase is made up of kataglacial (K_i) and anaglacial (A_i) parts; the same is true of the Glacials (K_g and A_g).

The passage from Interglacial to Glacial Phases was not characterised by continuous, uniform sedimentation. It consisted in warm interglacial sedimentation (A_i) and cold glacial sedimentation (A_g), separated by erosion phases (E_a), In the passage from Glacial to Interglacial Phases, the order was reversed.

To sum up the results of these considerations of a morphologic and climatic nature, it should be stressed once more that they are based on geologic data, i. e., on an accurate stratigraphy of quaternary deposits, chiefly of the River Wieprz and River Bug valleys. The action of these rivers was sedimentary and erosive and its fluctuations are clearly correlated with changes of climate. The erosion surfaces which divide the cold from the warm deposits are not of a local or sporadic nature, but, being encountered over considerable areas, have a general significance. Hence their great stratigraphic importance. An erosion surface may, on close investigation, become a stratigraphic index horizon, no less essential and important than the sedimentary levels.

This is a point of a paleomorphological nature which the author particularly wishes to stress.

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